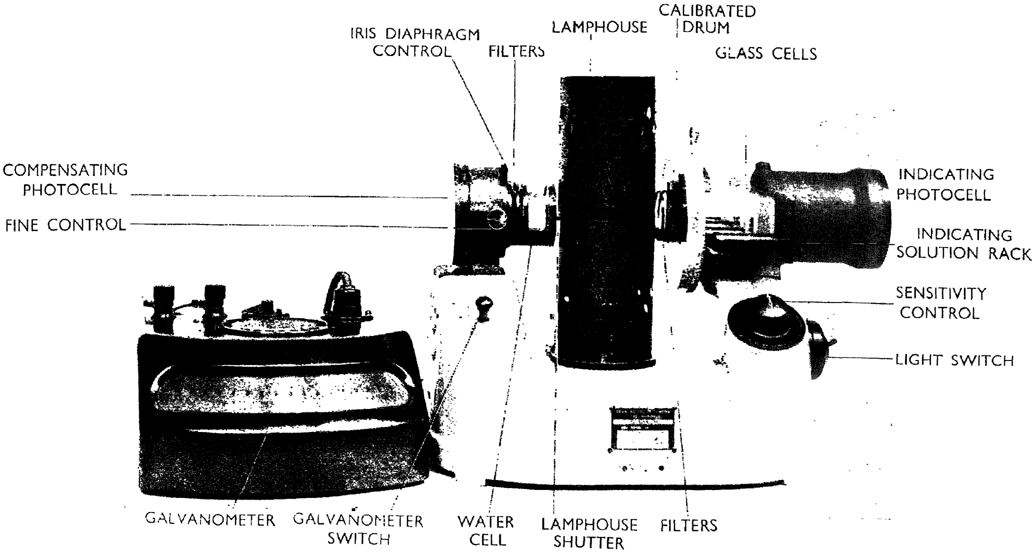

Fig. 1. The Spekker Photo-electric Absorptiometer.

METALLURGICAL ANALYSIS

BY MEANS OF THE

SPEKKER PHOTO-ELECTRIC ABSORPTIOMETER

by

F. W. HAYWOOD, Ph.D., F.I.C.
Chief Metallurgist
Messrs Wild-Barfield Electric Furnaces, Ltd.

and

A. A. R. WOOD
Research Chemist
Messrs Wild-Barfield Electric Furnaces, Ltd.

ADAM HILGER, LIMITED
98 ST PANCRAS WAY, CAMDEN ROAD
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Foreword

In colorimetric analysis the measurement is made by matching the colour of the solution under test with that of a solution of known strength. Although the instruments by which this is done do not *measure* colour, the name "colorimeter" is not inappropriate. When, however, a photo-electric cell is introduced to replace the eye, "colorimeter" becomes a misnomer, and the instrument described by the authors is called an "absorptiometer."

The action of the absorptiometer is described in the text; briefly, the proportion of radiation absorbed by the solution under analysis is measured for various known strengths and a graph plotted. Thereafter no standard solutions are needed. By limiting with a colour filter the portion of the spectrum utilised, additional possibilities of analysis are opened up. These have been exploited by Vaughan and his collaborators at the Admiralty Inspection Laboratory, Sheffield, to determine several constituents successively in one and the same solution made from a single weighing.

Although Vaughan's technique is of such recent introduction (his first paper was only published in 1941) the authors have been able to collect a very impressive number of analytical procedures which cannot fail to be of the greatest use to metallurgists.

Colour filters have been used also in visual colorimeters, but, as the authors point out, the accuracy obtainable with visual instruments is insufficient for the determination of the major constituents of an alloy, and colorimetric analysis has, therefore, been mainly limited to those constituents present in small proportions.

It is difficult to discontinue the use of a name which has once been firmly established, but the phrase "colorimetric analysis" as applied to the new technique is very unsuitable, and the distinction between the visual and photo-electric types of measurement is likely to become more pronounced in the course of time. The authors are therefore well justified in using the phrase "absorptiometric analysis" for determinations made by this instrument, even where the chemical technique is similar to, or identical with, that previously used with visual colorimeters.

Analysis in metallurgical laboratories used to be chiefly concerned with passing metals and alloys to specification. Physical methods of analysis which have come into vogue within the last two decades enable control to be exercised more promptly; in some cases the chemist is able to intervene early enough to correct the product without interruption of the process. Absorptiometric analysis is among the methods to which this enhanced degree of control is due.

The improvements in these physical methods have been so numerous in recent years as to justify the hope that the metallurgist may before long be able so to check all the processes from ore to finished alloy as to *ensure* the correctness of the latter, and thus to render test to specification superfluous. This book, which makes details of the new technique conveniently accessible, will be a notable aid to such full control.

F. TWYMAN.

29*th December* 1943.

Preface

As the result of numerous inquiries from users of the Spekker Photo-electric Absorptiometer in industry for collected data on the manipulation and use of the instrument and of the methods available for metallurgical analysis, this book has been written. It is hoped that it will provide in some small measure this information for those already engaged in industry in this kind of work ; guidance to those giving consideration to the application of such methods in routine control, and as an indication to research workers of the many problems still to be solved in the application of absorptiometric methods to metallurgical analysis.

The book is divided into two main sections ; the first section dealing with the functions, manipulation, and operation of the instrument ; the second with methods of metallurgical analysis as applied to standard engineering alloys ; most of these methods having been developed during the last three or four years. Only those methods which have been proved trustworthy in industry are included ; this does not imply that this section is complete ; it should be taken merely as indicative of the scope of the work. No attempt has been made to give references throughout the book, largely owing to the scarcity of them ; but the reader is referred to Chapter IV. where a brief survey of the most important papers and books of reference on Absorptiometry are collected.

The pioneer work on the use of the Absorptiometer in metallurgical analysis is due to Mr Vaughan and his collaborators who developed much of the technique used in this type of work. The authors wish to acknowledge their indebtedness to Mr Vaughan for his kind consideration and lively interest displayed on all occasions.

Our especial thanks are due to Mr F. Twyman, F.R.S., Managing Director of Messrs Adam Hilger, for advice, guidance, and helpful criticism, and not least for the foreword to this book.

To our many friends in industry who have willingly supplied numerous samples of all types of ferrous and non-ferrous alloys, we tender our grateful thanks. These are too numerous to mention individually, but especial mention must be made of the help and collaboration of Mr F. Harrison, who has assisted with much of the work given under magnesium alloys. Our thanks are also due to Mr E. S. Dreblow and other members of the staff of Adam Hilger for many helpful suggestions, and particularly to Mr T. L. Tippell for the preparation of the index.

In addition to our obligations to the printers, we must express our gratitude and indebtedness to the following :—

To the Directors of Messrs Wild-Barfield Electric Furnaces, Ltd., Watford, for permission to publish the results of work carried out in their laboratory, and for their unfailing support and encouragement at all times.

To Mr P. S. Richardson and Mr C. I. Anderson of the staff of Wild-Barfield Electric Furnaces, Ltd., for the preparation of the illustrations.

F. W. H.
December 1943. A. A. R. W.

CONTENTS

PART I

THE SPEKKER PHOTO-ELECTRIC ABSORPT
ITS MANIPULATION AND SCOPE

CHAPTER PAGE

I. GENERAL PRINCIPLES OF COLORIMETRIC ANALYSIS . 1
Historical introduction—Theory of Spectrophotometry—Photometers.

II. THE SPEKKER PHOTO-ELECTRIC ABSORPTIOMETER . 6
General description—Light sources and selectivity.

III. OPERATION OF THE ABSORPTIOMETER . . . 12
Position—Electrical connections—Setting of instrument—Calibration—Glass cells.

IV. DISCUSSION AND POSSIBLE FUTURE DEVELOPMENTS . 29
Advantages and limitations of absorptiometric methods of analysis—Accuracy — Time — Apparatus — Possible future developments—Literature—Conclusions.

PART II

SOME ABSORPTIOMETRIC METHODS OF ANALYSIS

V. ANALYSIS OF FERROUS ALLOYS 39
Introduction—Determination of chromium, cobalt, copper, manganese, molybdenum, nickel, silicon, titanium and vanadium—Composite scheme of analysis.

VI. ANALYSIS OF COPPER ALLOYS 76
Introduction—Determination of copper, iron, manganese, nickel and phosphorus—Composite scheme of analysis.

VII. ANALYSIS OF ALUMINIUM ALLOYS 92
Introduction—Determination of copper, iron, manganese, nickel, silicon, and titanium—Composite scheme of analysis.

VIII. ANALYSIS OF MAGNESIUM ALLOYS 110
Introduction—Determination of aluminium, copper, iron, manganese, and silicon—Composite scheme of analysis.

NAME INDEX 125

SUBJECT INDEX 126

LIST OF ILLUSTRATIONS

PART I

FIG. PAGE

1. The Spekker Photo-electric Absorptiometer . *Frontispiece*
2. Photo-electric diagram of the Spekker Photo-electric Absorptiometer 7
3. The two light sources in common use with the Absorptiometer 8
4. General layout of instrument and fittings for routine metallurgical analysis 13
5. Electrical wiring diagram using the tungsten lamp . 15
6. Electrical wiring diagram using the mercury lamp . 15
7. Calibration graphs for **MANGANESE** in ferrous alloys, using the tungsten lamp 24
8. Calibration graphs for **MANGANESE** in ferrous alloys, using the mercury lamp 25

PART II

9. Calibration graph for **CHROMIUM** (0–0·25 per cent.) in ferrous alloys 42
10. Calibration graph for **CHROMIUM** (0–3·0 per cent.) in ferrous alloys 45
11. Calibration graph for **COBALT** in ferrous alloys . . 49
12. Calibration graph for **COPPER** in ferrous alloys. . 54
13. Calibration graph for **MOLYBDENUM** in ferrous alloys 60
14. Calibration graph for **NICKEL** in ferrous alloys . . 64
15. Calibration graph for **SILICON** in steels 67
16. Calibration graph for **TITANIUM** in ferrous alloys . 70
17. Calibration graph for **VANADIUM** in ferrous alloys . 73
18. Composite scheme of analysis for Cr, Co, Cu, Mn, Mo, Ni, Si, Ti, and V in ferrous alloys 74
19. Calibration graph for **COPPER** in copper alloys . . 77
20. Calibration graph for **IRON** in copper alloys . . . 81
21. Calibration graph for **MANGANESE** in copper alloys . 84
22. Calibration graph for **PHOSPHORUS** in copper alloys 90
23. Composite scheme of analysis for Cu, Fe, Mn, Ni, and P in copper alloys 91

FIG. PAGE
24. Calibration graph for **IRON** in aluminium alloys . 96
25. Calibration graph for **SILICON** in aluminium alloys . 105
26. Calibration graph for **TITANIUM** in aluminium alloys 108
27. Composite scheme of analysis for Cu, Fe, Mn, Ni, Si, and Ti in aluminium alloys 109
28. Calibration graph for **ALUMINIUM** in magnesium alloys 111
29. Calibration graph for **COPPER** in magnesium alloys . 115
30. Calibration graph for **IRON** in magnesium alloys . . 118
31. Calibration graph for **SILICON** in magnesium alloys . 123
32. Composite scheme of analysis for Al, Cu, Fe, Mn, and Si in magnesium alloys 124

LIST OF TABLES

NO. TITLE.
I. Ilford Spectrum Filters—Values of Percentage Transmission 10
II. Wave-lengths of principal lines emitted by Mercury . 11
III. Filters for use with Mercury Vapour Lamp . . . 11
IV. Conversion table taken from a calibration graph . . 23
V. Methods available for dilution 33

Metallurgical Analysis by Means of the Spekker Photo-electric Absorptiometer

PART I

CHAPTER I

GENERAL PRINCIPLES OF COLORIMETRIC ANALYSIS

Introduction

THE measurement of the intensity of colour of a coloured solution has been used in analysis for well over a century. One of the earliest methods evolved was the estimation of ammonia by Nessler, using alkaline solutions of potassium-mercuric iodide. This, although possibly the best known historical example, is not the first recorded method using colorimetric principles. Keates in 1830 produced a method for the estimation of copper; Ossian in 1837 a method for iron using potassium thiocyanate; and Lampadius in 1838 a method for cobalt in minerals using the brown coloration produced by ammonia. Since that time many and varied colorimetric methods have been produced in all branches of chemistry, but in every case the final measurement involved the use of the unaided human eye for the comparison of the intensity of the colour. Instruments termed colorimeters were used to determine these intensities, but it is not within the scope of this book to discuss the various colorimeters which have been employed for this work. The reader is referred to the standard treatises and works on this subject, some of which are given in Chapter IV.

In most early colorimetric work, and indeed until recent years, it has been necessary to separate interfering elements prior to the coloration of the element or radical sought, or to produce the colour and separate by solvent action. Not infrequently, standard gravimetric processes involving precipitations, extractions and the like were absolutely essential before a given element was determined by colorimetric means. Such processes were time consuming and introduced certain unavoidable errors. The scope of ordinary colorimetric analysis was restricted owing to the fact that, even when using colorimeters, a high degree of accuracy was not obtainable. Because of this fact, and the high sensitivity frequently obtained with certain colours, colorimetric methods were almost entirely confined to the analysis of traces of elements.

Colorimetric analysis is based upon the variation in colour in a system due to a change in concentration of some component. The colour is generally due to the production of a coloured compound by the addition of a specific chemical reagent or it may be a property of the desired radical itself. A few examples will illustrate these points. Iron may be determined in solution by the addition of potassium thiocyanate to produce the blood red ferric thiocyanate; manganese may be oxidised by the addition of a suitable oxidising agent in acid solutions to form the purple coloured permanganic acid; copper determined as the blue cuprammonium compound by the addition of an excess of ammonium hydroxide and phosphorus determined by the formation of the phospho-molybdate complex and subsequent reduction by stannous chloride to molybdenum blue. The above are varied examples of the addition of a specific chemical reagent. On the other hand certain compounds are inherently coloured, for example the yellowish-brown colour obtained when a straight carbon steel is dissolved in nitric acid, which serves to estimate the carbon content of the steel by the well-known Eggertz's method.

Photometric chemical analysis, of which colorimetric analysis forms a special branch, embraces all methods of analysis which are based upon the measurement of the quantity of light absorbed by a coloured solution. In colorimetry, white light, either natural or artificial, is used, the determinations being carried out in a colorimeter or visually. In spectrophotometry, light of a definite wave length or restricted spectral wave band, which may extend into the ultra-violet region of the spectrum, is employed and the determinations made with a spectrophotometer either visually or photo-electrically.

Theory of Spectrophotometry

Quantitative measurements of light absorption are founded on two fundamental laws, which concern the relationship between the intensities of the light incident upon a layer of an absorbing medium and the light transmitted by this medium.

(1) Lambert's Law

In 1760 Lambert investigated the relationship between the incident and transmitted light and stated that the proportion of light absorbed by a substance is independent of the intensity of the incident light. The law may also be stated in another form, namely, that each successive layer of the medium absorbs an equal fraction of the light passing through it. This is expressed in the form of an equation:

where I_0 is the intensity of the light entering the medium, I the intensity of the transmitted light, l the thickness of the absorbing medium, and a a constant known as the "absorption coefficient" of the substance. The constant more generally employed is the "extinction coefficient" which was defined by Bunsen and Roscoe (Pogg. Ann., Vol. 177, p. 238) in the following manner: "Let I_0 be the intensity of the incident light which enters the medium, I the intensity remaining after its subsequent passage through a path length l, and $\frac{I}{K}$ the path length, passage through which reduces the light intensity to 1/10th; then

$$I=I_0 . 10^{-Kl}$$

where K, a constant depending on the medium, is called by us the 'extinction coefficient,' l being measured in centimetres." Thus it will be clear that the extinction coefficient of Bunsen and Roscoe is the reciprocal of the thickness of the medium necessary to weaken the light to 1/10th of its original incident value. It is represented by K which is related to the absorption coefficient a by the equation :—

$$a=(\log_e 10)K=2{\cdot}3026K.$$

(2) Beer's Law (1852)

This law states that the absorption is proportional to the number of molecules of the absorbing medium through which the light passes. If the absorbing substance is dissolved in a non-absorbing medium, then the absorption will be proportional to the concentration of the solution. If I_0 is the intensity of the light entering the solution, I that after passage through a thickness of solution equal to l centimetres, and c is the concentration, the law may be expressed as :—

$$I=I_0 . \alpha^{-cl}$$

where α is a constant for the absorbing solution and is the ratio of the transmitted to incident intensity for a thickness of unity and unit concentration.

If ϵ is written for K/c, the second expression for Lambert's law using the extinction coefficient becomes :—

$$I=I_0 10^{-\epsilon cl}$$

Expressed in words this means that the extinction coefficient K, for a given wave-length, of a solution of concentration "c," is c times that of a solution of unit concentration, while for a given substance cl is constant for a given ratio of I to I_0. When c is in gramme-molecules of absorbing substance per litre of solution, ϵ becomes a measure of the absorption due to a single molecule and is then known as the "molecular extinction coefficient." This quantity is most conveniently employed when comparing the absorption spectra of different substances.

It may be well before proceeding to photo-electric absorptiometers and similar instruments, to summarise the essential nomenclature used in absorption spectrophotometry :—

I_0=intensity of the light entering the absorbing medium.
I =intensity remaining after passage through a length l.
l =length of path in centimetres.
c =concentration of the absorbing substance in solution expressed in the usual terms of gramme-molecules per litre.
K is the extinction coefficient defined by the expression $I=I_0 10^{-lk}$.
ϵ is the molecular extinction coefficient defined by the expression $I=I_0 10^{-\epsilon cl}$.
a is the absorption coefficient defined by the expression $I=I_0 e^{-al}$.
To these may be added d, the density$=\log_{10}(I_0/I)$. Density$=lK$.

Beer's Law has been found to hold over a considerable range of concentration for a large variety of coloured compounds and this law is the basis of most colorimetric determinations. When a substance does not follow Beer's Law, the cause should be sought in some change in the absorbing molecules rather than by assuming that the law is invalid.

Spectrophotometers

As mentioned in the introduction, colorimeters employ natural or artificial white light for the measurement of the intensity of colour of a solution, that is the quantity of light absorbed by a solution, whereas spectrophotometers employ a restricted spectral wave-band of light. Although instruments of the latter type have been in use for many years, the practical application to standard metallurgical chemistry has been confined to a relatively small number of such instruments. It is only intended to mention one of the visual type of spectrophotometers and to confine the remainder of the book, as its title implies, to a study of the Spekker Photo-electric Absorptiometer.

The first instrument applied to metallurgical analysis and using a restricted spectral wave-band was the Zeiss-Pulfrich Photometer, which, however, suffers from the same defect as colorimeters, in that the final measurement relies entirely upon matching two adjacent fields of view with the human eye. The general arrangement of the Pulfrich Photometer consists of a common light source diverged to form two parallel paths of light which each pass through condensing lenses, glass cells of equal dimensions (to contain water and solutions), variable calibrated apertures and finally, after passage through lenses, suitable prisms, a biprism and appropriate filter, fall on the ocular and the eye of the observer. One cell contains water and the other the coloured solution under examination. A reading is taken by adjusting the calibrated aperture appertaining to the water cell, until the two halves of the field of view are matched. By reference to a calibration graph or a factor, the percentage of the particular element can be determined.

The use of photo-electric cells enables the light transmitted through solutions to be converted to electrical energy, and thus measurements can be made using an electric circuit with a galvanometer whose null point corresponds with equal E.M.F. from two cells. This principle is employed in the Spekker Photo-electric Absorptiometer. Not infrequently photo-electric instruments used for photometric analysis are termed "photo-electric colorimeters," a misnomer, as they measure not the colour but the absorption of the solution. It is preferable to refer to such instruments as "photo-electric absorptiometers," and this nomenclature will be adhered to throughout this book.

CHAPTER II

THE SPEKKER PHOTO-ELECTRIC ABSORPTIOMETER

THE Spekker Photo-electric Absorptiometer is an instrument which differs from the Pulfrich and like photometers, in that the final measurement is not made by the human eye, but by means of photo-electric cells and a galvanometer. A light source, which may be a tungsten filament lamp or a mercury vapour lamp, provides two light paths which both pass successively through special colour filters, variable apertures, cells containing either water or solution, condensing lens systems, and finally on to two photocells. The photocells are connected in opposition in a null point circuit, across a galvanometer. When equal quantities of light are falling on each photocell a null deflection results on the galvanometer. When, however, unequal quantities of light fall on the photocells, as in the case of light passing through a coloured solution producing consequent absorption of some of the light, a definite deflection is obtained on the galvanometer. In order to bring the reading on the latter back to zero, it is necessary to allow more light to pass through the coloured solution. This is effected by means of a calibrated variable aperture, the reading of which provides a measure of the light absorption of the solution and, consequently, of the concentration of the coloured constituent in the solution.

Fig. 1 shows the Spekker Photo-electric Absorptiometer and mirror spot type galvanometer, this being the standard equipment necessary for accurate metallurgical analysis.

A diagrammatic layout of the Spekker Photo-electric Absorptiometer together with the photo-electric details is shown in Fig. 2. The light source is situated approximately in the middle of the instrument, and is surrounded by a metal lamp housing designed to allow free circulation of air. The lamp is operated by a switch on the right-hand side of the instrument (see Fig. 1), whilst a shutter on the lamphouse is provided to interrupt the passage of light through two apertures to the left and right of the lamphouse. To the right of the lamphouse, *i.e.* towards the indicating photocell, light passes successively through a colour filter contained in a rack, a variable calibrated aperture and a lens which converges the light to a parallel beam. The aperture is a rectangular slit and is operated by the vertical movement of the lower component of the slit. The movement of this shutter is actuated by means of a large diameter drum calibrated between 0 and 3·0, being calibrated logarithmically in order that a reading shall be proportional to the opening of the aperture. To the right of the drum is a movable rack for the glass cells containing either water or solutions ;

three cells being accommodated at a time and each one capable of being moved into the path of light by traversing the rack into the appropriate position. Light is subsequently converged by passing through a lens and finally falls on the indicating photocell which is mounted in the housing seen on the extreme right of the instrument and above the light switch in Fig. 1.

To the left of the lamphouse, the light passes through a glass cell containing water, a filter of the same colour and density as that on the indicating side; and finally through a variable aperture (which is not calibrated) on to the compensating photocell. This aperture consists of an iris diaphragm operated by the iris diaphragm control. In conjunction with the iris diaphragm is a fine control for the passage of light, consisting of a cam-shaped rod at right angles to the direction of the light; thus small differences in the amount of light falling on the photocell may be made with this device.

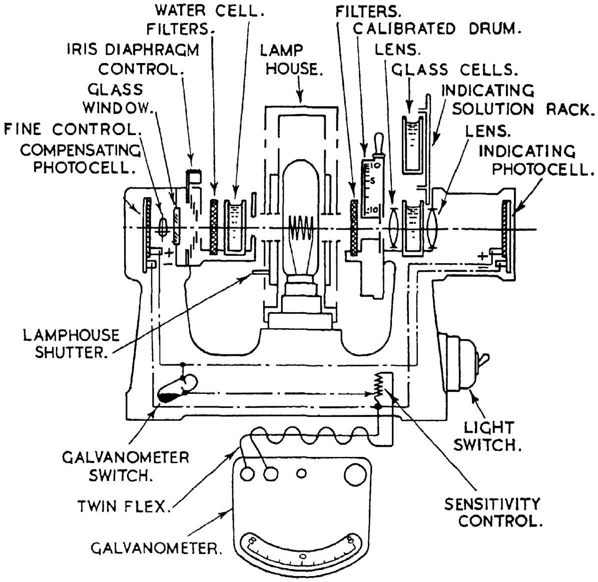


FIG. 2. General arrangement of the Spekker Photo-electric Absorptiometer showing the photo-electric circuits.

A mercury switch for the photo-electric connections is located in front of the compensating photocell on the left-hand side of the instrument, and by depressing this switch the circuit is made. Finally, the sensitivity control, which is situated on the right-hand side of the instrument, in a corresponding position to that of the galvanometer switch, acts as a variable shunt across the galvanometer. It consists of a circular variable resistance and its function may be seen clearly in Fig. 2.

Light Sources

Light selectivity plays a very important part in modern photometric methods of metallurgical analysis. The Absorptiometer in its current form is fitted with two alternative light sources, namely a tungsten filament and a mercury lamp, both of which have to be used with colour filters transmitting light over restricted spectral wave-bands. These are now to be dealt with in detail.

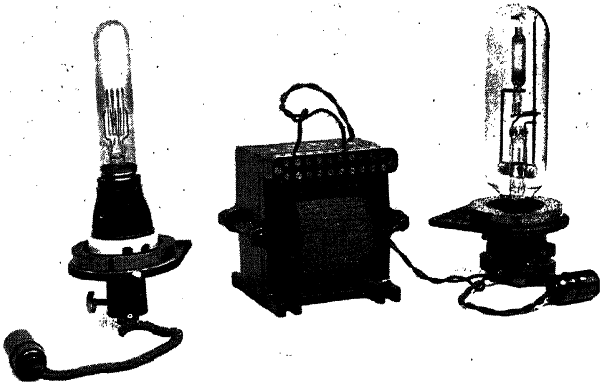


FIG. 3. The two light sources in common use with the Absorptiometer.

Tungsten Filament Lamp

This lamp is shown to the left-hand side of Fig. 3. It is a standard flat filament projection lamp, the heated element being of the grid type and is normally of 100 W. output. If white light only is used in the Absorptiometer the sensitivity is low, since the percentage of light absorbed is low compared with the incident light. Now all coloured solutions absorb light in a specified region or regions of the spectrum, and it is for this reason that a solution appears coloured. Thus with a solution of potassium dichromate, which is orange coloured, light in the violet portion of the spectrum (4000–4500) is absorbed and the majority of the light transmitted and observed is in the yellow-orange region (5500–6000). For this reason the use of a blue or violet filter will give maximum sensitivity for yellow-orange solutions. This reasoning applies equally for any coloured solution.

The action of the colour filters can be illustrated by reference to absorption figures taken on an actual determination, namely that of copper as the copper diethyldithiocarbamate complex, with and without the use of the appropriate colour filters. Two solutions were made up, one containing exactly 10 per cent. more of the complex than the other and the absorptions measured with and without the use of Ilford Spectrum Blue filters No. 602. Results were obtained as follows :—

Without filter—	Transmission.	Density.
Initial concentration of copper complex S_1 .	0·60	$0{\cdot}22_2$
Increased concentration of copper complex $1{\cdot}1S_1$	0·59	0·23
Using Ilford Spectrum Blue filters No. 602—		
Initial concentration of copper complex S_1 .	$0{\cdot}14_1$	0·85
Increased concentration of copper complex $1{\cdot}1S_1$	$0{\cdot}11_6$	0·93

It will be obvious, from the last column of this table, that a much greater sensitivity to change in concentration is obtained by the use of a colour filter, and taking the usual limit of measurement on the drum as 0·005, it will be seen that the difference in concentration of the two solutions, namely 10 per cent., can be determined with an accuracy of 0·6 per cent., whereas without the use of filters the accuracy is 6 per cent.

The Absorptiometer is supplied with eight pairs of coloured filters termed Ilford Spectrum filters, and one pair of Chances "Calorex" heat absorbing filters. All are carefully matched for colour and density and are suitably marked as :—

R—for use on the right-hand side of the instrument, *i.e.* indicating side.

L—for use on the left-hand side of the instrument, *i.e.* compensating side.

The filters to be used for specific determinations are given in Part II, and in each case the filters are chosen to give optimum sensitivity. When dealing with unknown solutions it will be found necessary to try each pair of filters in turn, using that pair for the determination which give a suitable or maximum sensitivity.

The complete set of Ilford Spectrum filters is numbered 601 - 608 and is of a gelatine type between glass plates. The approximate transmission data for these filters are given in Table I.

TABLE I—**Ilford Spectrum Filters**

Values of Percentage Transmission ($=T\times 100$)

Wave-length in Angstrom Units.	Violet 601	Blue 602	Blue-Green 603	Green 604	Yellow Green 605	Yellow 606	Orange 607	Red 608
3500	—	—	—	—	—	—	—	—
3600	—	—	—	—	—	—	—	—
3700	—	—	—	—	—	—	—	—
3800	0·3	—	—	—	—	—	—	—
3900	2·1	—	—	—	—	—	—	—
4000	8·7	—	—	—	—	—	—	—
4100	18·0	—	—	—	—	—	—	—
4200	27·0	—	—	—	—	—	—	—
4300	29·0	—	—	—	—	—	—	—
4400	24·0	0·3	—	—	—	—	—	—
4500	16·0	2·1	—	—	—	—	—	—
4600	7·2	9·8	—	—	—	—	—	—
4700	1·5	14·0	—	—	—	—	—	—
4800	0·1	8·5	6·3	—	—	—	—	—
4900	—	3·4	12·0	—	—	—	—	—
5000	—	0·7	8·3	1·4	—	—	—	—
5100	—	—	5·0	7·2	—	—	—	—
5200	—	—	0·7	10·0	—	—	—	—
5300	—	—	0·1	4·8	0·7	—	—	—
5400	—	—	—	1·6	3·9	—	—	—
5500	—	—	—	0·3	5·5	—	—	—
5600	—	—	—	—	4·2	1·6	—	—
5700	—	—	—	—	1·5	5·9	0·1	—
5800	—	—	—	—	0·3	7·2	2·8	—
5900	—	—	—	—	—	4·9	9·6	—
6000	—	—	—	—	—	2·4	19·0	—
6100	—	—	—	—	—	1·0	13·0	0·1
6200	—	—	—	—	—	0·4	8·7	0·7
6300	—	—	—	—	—	0·2	5·8	3·0
6400	—	—	—	—	—	—	4·3	6·0
6500	—	—	—	—	—	—	3·2	13·0
6600	—	—	—	—	—	—	2·4	16·0
6700	—	—	—	—	—	—	1·7	19·0
6800	—	—	—	—	—	—	1·2	20·0
6900	—	—	—	—	—	—	0·7	20·0
7000	—	—	—	—	—	—	0·4	20·0

Mercury Lamp

This lamp, together with its choke, is shown on the right-hand side of Fig. 3. This is a normal type of mercury vapour lamp working on 110 volts A.C. supply. This lamp has been applied to absorptiometric metallurgical analysis—using the Absorptiometer—by reason of the fact that the light emitted consists of a definite number of spectrum lines. The colours and wave-lengths of these lines are as follows :—

TABLE II—**Wave-lengths of Principal Lines emitted by Mercury**

Colour.	Wave-lengths.
Yellow	5790 – 5770
Yellow-Green	5460·7
Blue-Green	4916
Blue	4358·35 – 4339·24
Violet	4007·8 – 4046·56
Ultra-Violet	3663·27, 3654·83, 3650·15
Ultra-Violet	3341·48

It is at once obvious that a greatly increased light selectivity is obtained by using spectrum lines available. Only those solutions absorbing light included in this table will give readings on the Absorptiometer ; those which do not, will behave like colourless solutions and will give no readings at all. In not a few instances, therefore, the mercury vapour lamp has distinct advantages over the tungsten lamp in that sometimes a difference method need not be applied. On the other hand, by reference to other methods given in Part II, it will be noticed that certain determinations cannot be carried out using this lamp owing to the absence of appropriate spectrum lines.

The set of filters provided for use with this lamp are as follows :—

TABLE III—**Filters for Use with Mercury Vapour Lamp**

Wave-length of Hg. Line.	Filters, Heat Absorbing.	Filters, Colour.
5770–5790	Calorex	Ilford Spectrum Yellow No. 606
5460·7	Calorex	Ilford Spectrum Yellow-Green No. 605 or Kodak No. 74
4358·35	Chance No. 6	Wratten No. 50
4077·8 4046·56	Chance No. 8	Wratten No. 2
3650	None	Wood's Glass

CHAPTER III

OPERATION OF THE INSTRUMENT

Position of Instrument

THE instrument should be kept in a room set apart for the purpose or alternatively in an instrument or dark room, this being essential to exclude the presence of fumes which would be liable to corrode various parts of the instrument and fog the glass surfaces of lenses and cells.

If possible an allotted amount of bench space should be available for the filling and storing of cells, together with tap and distilled water and drainage supply, for adequate cleaning of cells.

It will be appreciated from what has already been said about the Absorptiometer that light reaching the photocells from any but the light source itself will affect the reading. The instrument should be housed in a room where extraneous light is constant in intensity and position. Sunlight, for instance, should not be permitted to fall on the instrument, since variations in readings will be obtained on a cloudy or a bright day, or due to the movement of the operator in front of the instrument. The instrument needs to be checked before a calibration, to see whether variations in the extraneous light affect the drum reading. For the same reason, if the instrument has to be moved from one position to another in the same room, slightly different readings may be obtained and a fresh calibration would have to be made.

The Absorptiometer, galvanometer, and ancillary equipment may be conveniently housed in a cabinet (see Fig. 4), thus keeping the apparatus free from dust and fumes. Shelves are incorporated to house colour filter rack, cell rack, and other equipment. Appropriate space is available in the cabinet for calibration graphs, conversion tables, cleaning cloths, and the like.

Cleaning of Instrument

The cleaning of the instrument is absolutely essential if repetitive and reliable results are to be obtained. It will be appreciated that any obstruction to the path of light will cause a difference in drum reading, and the following precautions should be taken at all times if accurate results are to be obtained :—

(1) Dry glass surfaces should be cleaned with a dry selvyt cloth, and this type of cloth should never be used in the moistened condition.

(2) Damp or wet glass surfaces should be dried and cleaned with best quality chamois leather.

The following should also be borne in mind and should become a matter of strict routine, as it is only by scrupulous attention to seemingly trivial details that the Absorptiometer can function with entire satisfaction. Thus before using the instrument it is essential to:—

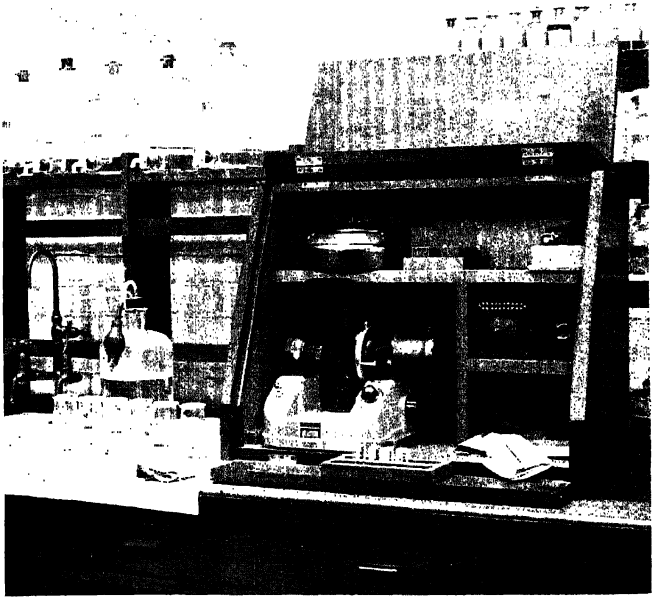


FIG. 4. General lay-out of instrument and fittings for routine metallurgical analysis.

(*a*) Remove dust from all surfaces with the minimum of disturbance.

(*b*) Carefully polish the two lens surfaces; one on either side of the indicating solution rack.

(*c*) Polish any colour filters which may be employed.

(*d*) Polish the outside surfaces of the two water cells.

When the instrument is not in use it is essential to:

(*a*) Close both apertures—the indicating calibrated aperture by setting the drum at a reading of infinity.
(*b*) Remove colour filters.
(*c*) Remove all glass cells.
(*d*) Close the lamphouse shutter.
(*e*) Keep the case shut.

If the instrument is in constant use, say 6 to 8 hours per day, for example, then occasionally—perhaps about once per month—the lamphouse should be removed and the lamp cleaned. When removing and replacing the lamp great care should be taken and the instructions given on this page followed strictly.

Electrical Connections and fitting of Light Sources

The Absorptiometer is supplied suitable for the normal single phase A.C. supply—200 - 250 volts—which is suitable for the tungsten lamp and, with the incorporation of a choke, for the mercury lamp. D.C. supply can be used only with the tungsten lamp.

Tungsten Lamp

The only electrical connections necessary are to the Absorptiometer and the galvanometer, which can be conveniently made from the same mains switch. It will be seen that two sockets are fitted on the back of the instrument; the mains connection is made to either of these, and the plug from the lamp housing to the other. The diagram of electrical connection is shown in Fig. 5.

Mercury Lamp

The mercury lamp works on any single phase A.C. supply above 190 volts. The current in the lamp, operating on 200-250 volt supply, is controlled by the use of a suitable choke. This choke may be housed conveniently behind the Absorptiometer, mounted on rubber supports if necessary. The diagram of electrical connections for the mercury vapour lamp is shown in Fig. 6. Besides the plug to the mains supply, there are two additional leads from the special lamp seating for the mercury lamp. One lead should be inserted in the zero fitting of the choke and the other in the terminal appropriate to the single phase A.C. mains supply available.

When using the mercury lamp it is necessary to switch on and allow the lamp to warm up for at least three minutes before any readings are taken, as maximum light intensity is not obtained immediately.

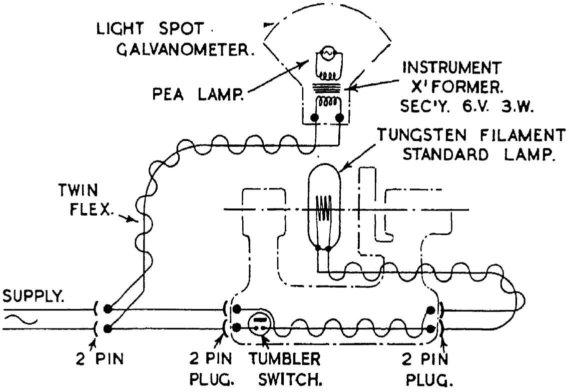


FIG. 5. Diagram of electrical connections using the Tungsten Lamp.

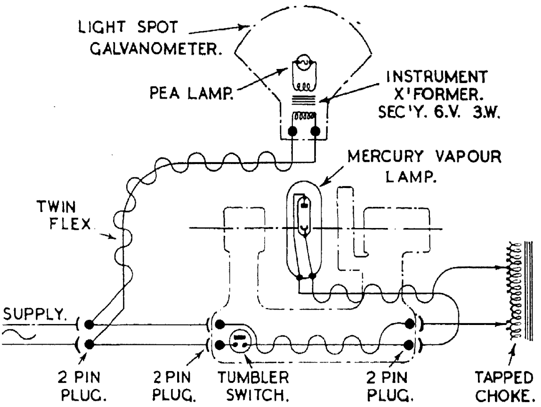


FIG. 6. Diagram of electrical connections using the Mercury Vapour Lamp.

After 3 minutes the light intensity changes only very slightly and no further change is perceptible after 7 minutes. If the lamp is now switched off it will not relight until it has cooled. This may take 15 to 20 minutes.

Setting of Instrument

Reference should be made to Figs. 1 and 2, as this will facilitate appreciation of this next section. Having cleaned all glass surfaces and made the requisite electrical connections, the instrument is set as follows :—

The cleaned water cell marked *W* is filled with distilled water and placed in the fixed rack in front of the compensating photocell. A 1 cm. glass cell is also cleaned, filled with distilled water and placed in the indicating solution rack, together with an appropriate sized cell containing the solution for analysis. These two glass cells are in adjacent compartments of the indicating solution rack. The next series of operations is as follows :—

(*A*) (1) Adjust the indicating solution rack so that the coloured solution is directly in the path of light.
(2) Place the appropriate colour filters in the right and left-hand filter racks, together with the heat absorbing filters, these latter always being nearer to the lamp.
(3) Adjust the indicating drum to zero.
(4) Close the compensating iris diaphragm completely.
(5) Adjust the sensitivity control to the minimum position.

(*B*) (1) Switch on the light source.
Note.—In the case of the light source being a mercury lamp allow a minimum time of 3 minutes to elapse before the next operation, when first switching on the lamp.
(2) Open the lamphouse shutter.
(3) Close the photo-electric circuit by depressing the galvanometer switch, and simultaneously rotate the sensitivity control until the galvanometer shows a maximum reading of 8.
(4) With the galvanometer switch still depressed, open the compensating iris diaphragm with a smooth movement, so as to bring the galvanometer reading back to zero. This final adjustment will have to be made with the fine control on the iris diaphragm.
(5) Close the lamphouse shutter.

(6) Move the indicating solution rack so that the indicating water cell is now in the position formerly occupied by the coloured solution.

(7) Open the lamphouse shutter.

(8) Depress the galvanometer switch and a reading will be obtained on the galvanometer. Now close the indicating drum by a smooth movement to bring the galvanometer reading to zero.

The reading obtained on the drum is then proportional to the amount of light absorbed by a given thickness of solution used and hence to the concentration of the particular coloured constituent in the solution.

Briefly the whole series of operations outlined may be summed up simply as follows :—

The instrument is set at maximum sensitivity for the particular filters used and solution to be measured. Equal E.M.F.'s are set up in each photocell, resulting in a null deflection on the galvanometer. When the indicating water cell is introduced in the path of light, more light will fall on the indicating photocell, thus producing a deflection on the galvanometer. By closing the indicating drum and thus restricting the amount of light falling on the indicating photocell, equal E.M.F.'s are again obtained and a null deflection on the galvanometer results.

It will be realised that if a large number of solutions is to be analysed and therefore a large number of readings required, that the sequence of operations previously detailed will have to be repeated for each solution. This is time consuming and unnecessary, and by using a slightly modified procedure one setting of the instrument will suffice to obtain several readings using the same colour filters and solutions of different concentrations. This is accomplished by setting the indicating drum at a convenient point on the scale, for example 1·0, with reference to the indicating water cell, and obtaining a reading for the solution undergoing analysis. The setting used with reference to the water cell, generally referred to as the " water to water setting " or " water setting," may be selected for a variety of reasons. It will be seen that the drum is calibrated with a logarithmic scale and that accurate readings of the order of 0·005 to 0·010 of a drum division may be made only over the range of 0 to 1·30. Above this latter figure the scale cannot be calibrated with the same degree of accuracy as below it, and it is not common practice in metallurgical analysis ever to work above a water setting of 1·3. Furthermore, the sensitivity obtainable, that is the ratio of galvanometer deflection to divisions on the drum, is very low when working with a water setting of greater than 1·0–1·3. To a certain extent this is a function of the filters used and the characteristics of the photocells in the particular Absorptiometer. The water setting used will therefore depend upon these factors, but as a rule a setting of 1·0 may be taken as suitable for general use. The sequence of operations for setting the instrument for all routine metallurgical analyses is thus as follows :—

(*A*) (1) Adjust the indicating solution rack so that the water cell is in the path of light.
    (2) Place the appropriate colour filters in the right and left-hand filter racks, together with the heat absorbing filters in the position previously indicated.
    (3) Adjust the indicating drum to a reading of 1·0.
    (4) Close the compensating iris diaphragm completely.
    (5) Adjust the sensitivity control to the minimum position.

(*B*) (1) Switch on the light source.
    Note.—In the case of the light source being a mercury lamp allow a time of 3 minutes to elapse before the next operation, when first switching on the lamp.
    (2) Open the lamphouse shutter.
    (3) Close the photo-electric circuit by depressing the galvanometer switch and at the same time rotate the sensitivity control until the galvanometer shows a maximum reading of 8.
    (4) With the galvanometer switch still depressed, open the compensating iris diaphragm with a smooth movement so as to bring the galvanometer reading back to zero and finally adjust with the fine control of the iris diaphragm.
    (5) Close the lamphouse shutter.
    (6) Move the indicating solution rack so that the cell containing the solution is in the position formerly occupied by the water cell.
    (7) Open the lamphouse shutter.
    (8) Depress the galvanometer switch and open the indicating drum by a smooth movement to bring the galvanometer reading to zero.

The reading obtained on the indicating drum is subtracted from the original water setting, say 1·0, and this difference is proportional to the amount of light absorbed by a given thickness of solution used, and hence to the concentration of the coloured constituent in the solution.

Direct Readings

With some determinations it is only necessary to take one reading on a coloured solution, this reading being directly proportional to the concentration of the element sought. This is the case with the determination of manganese in a magnesium alloy, since no other elements produce measurable colours. In order to illustrate the direct method this example is given in detail :—

0·5 grm. of a magnesium alloy is taken into solution and the manganese oxidised to permanganic acid by the silver persulphate reaction in acid solution (see Part II, p. 120). The solution is made up to 100 ml. with water and the absorption of this solution measured using 1 cm. glass cell, Ilford Spectrum Green filters No. 604, and a water setting of 1·0 The results may be set out as :—

Alloy.	Drum Reading.	% Mn.
Mg. alloy	0·49	0·28

The drum reading of 0·49 is referred to a graph calibrated by the direct method, or alternatively to a table of figures, and the percentage of manganese read off directly.

Difference Reading

In many analyses it is necessary to take more than one reading on the same solution in order to obtain a figure which is strictly proportional to the concentration of the element sought. The reason for this is that whilst a particular element may be coloured up, there are other elements already in solution, which, although they do not react with the specific reagent producing the specific colour of the element sought, are inherently coloured. The absorptions of these solutions are additive and it is necessary, in order to obtain the absorption of the particular element, to account for all other coloured salts in solution. For example, when determining manganese in a steel, this element is oxidised to permanganic acid by the silver persulphate reaction in acid solution. The absorption due to manganese can be represented by A and that due to the other coloured salts in solution by B. Thus the absorption measured is $(A+B)$. By decolorising the permanganic acid the absorption due to the other coloured salts in solution, namely B, is obtained. Thus by subtracting these two readings, namely $(A+B)-B$, the value of A (the absorption due solely to manganese) is obtained.

A specific example is now given which illustrates this procedure. A 0·5 grm. sample of an 18/8 stainless steel is taken into solution and the manganese oxidised to permanganic acid by the silver persulphate reaction in acid solution (see Part II, p. 119). The solution is made up to 100 ml. with water. It will be noticed that the resulting colour of this solution is bright red, owing to the dichromic acid which is produced in solution due to the same reaction; green nickel salts will also be in solution. The presence of these coloured salts will absorb light in addition to that absorbed by the permanganic acid, and thus a high reading is obtained. This reading is that previously represented in the preceding paragraph by $(A+B)$ and is obtained by measuring the absorption in 1 cm. glass cells, using Ilford Spectrum Green filters No. 604 and a water setting of 1·0. By adding one drop of sodium nitrite solution to the cell, the permanganic acid is decolorised without affecting the colour of the other salts in solution, and another reading is obtained under identical conditions. This reading, previously represented by B, gives the absorption due to these other coloured salts and is known as the " blank " reading. Thus by simple subtraction the absorption due solely to manganese is obtained. The results may be set out conveniently as follows :—

	Drum Readings.			
Sample.	Colour.	Blank.	Difference.	% Mn.
18/8 steel	0·32	0·83	0·51	0·28

The difference reading of 0·51 is referred to a graph calibrated for manganese by the difference method, or alternatively to a table of figures and the percentage of manganese read off directly.

It is not always possible to adopt the procedure outlined in the above example for obtaining the blank reading—in fact at the moment it is restricted to Mn—as many coloured complexes cannot be decolorised solely without affecting the other inherently coloured constituents of the solution. There are many methods used to obtain this blank reading and these are given in detail in Part II.

Calibration

In normal colorimetric analysis, the final measurement is made by comparing the intensity of the colour of the unknown solution with that of a standard solution of a known concentration. There are several methods by which this comparison can be effected, and a brief description is now given.

Balancing Method

Two similar graduated tubes are taken and into one is introduced the coloured solution of unknown concentration. To the other is added a measured volume of a standard colour solution, until the two solutions in the tubes are matched when viewed vertically. The concentration of the element producing the colour is inversely proportional to the height of liquid in the tubes.

Dilution Method

Again two similar graduated tubes are taken and the solution of unknown concentration placed in one of them. A definite amount of a standard solution is added to the other and the two tubes are viewed horizontally. The darker solution is diluted until the two tubes are matched. The volumes of solution in the tubes are then directly proportional to the concentration of the coloured component.

Duplication Method

The solution of unknown concentration is placed in a glass tube and made up to a definite volume. In a similar tube are placed the specific reagents producing the colour and diluted to nearly the same volume as the first tube. A concentrated solution of known strength and volume of the element producing the coloured complex is added to the second tube until the colours match when viewed vertically. The amount of the known element added must be equal to that present in the unknown solution.

Standard Series Method

A series of tubes containing varying known amounts of the coloured solution are taken and made up to a definite volume. The coloured solution of unknown concentration is then compared with the standards until a match is obtained. The concentration of the unknown solution is equal to that of the solution with which it is matched.

Calibration of the Absorptiometer

From the foregoing brief remarks it is obvious that to adopt any such procedure for photo-electric measurement would be a lengthy and tedious process. Furthermore, inaccuracies would be introduced apart from the fact that a standard solution is always necessary.

A modified form of the standard series method is used, in which a number of standards are produced and the absorptions measured under identical conditions to those appertaining in the method of analysis used for the particular element sought. In most calibrations, reagents of known analytical purity can be used for producing the standard solutions, and since only one set of standards is required for any given element, time can be afforded to prepare them accurately. The drum readings for these solutions are plotted on a graph against the concentration of the element present. In this manner the virtual equivalent of 200–300 measurable standards as used in the standard series method is obtained and in addition is quite permanent, so long as the instrument retains its initial characteristics. Once a calibration graph has been obtained, it is advisable to check this, say, once every six months, in case a slight change should occur owing to variations of the colour filters or the photocells.

"H.H.P." Metals and Alloys

As previously mentioned, the calibration of the Absorptiometer must be carried out with great care, using chemicals of only the best reagent quality procurable. Not infrequently, however, even when employing such reagents, it has been found necessary to standardise them before calibration. In order to obviate the necessity for such work and to provide materials which are more analogous to particular determinations, Messrs Adam Hilger have placed on the market a new range of materials termed " H.H.P." metals and alloys. These materials are all in the form of either turnings, drillings, millings, etc., and are of guaranteed purity and similar in form to alloys encountered in metallurgical analysis. They are put up especially for use with the Absorptiometer and their adoption still further decreases the overall time required to carry out specific determinations.

Whenever possible the use of " H.H.P." materials has been included in the determinations given in Part II.

It will be seen that in absorptiometric analysis the final measurement of the absorption of the constituent in solution is a function of :—

(1) Initial weight of the alloy taken.
(2) The concentration of the alloy in the solution to be measured.
(3) The thickness of the absorbing layer of solution, *i.e.* the length of glass cell chosen.

These points are illustrated by reference to the determinations and calibration for manganese in ferrous alloys (for full chemical details see Part II, p. 55). In the actual determinations 0·50 grm. of a ferrous alloy containing say 0·50 per cent. manganese is dissolved, suitably oxidised and made up to 100 ml. with water. The absorption of such a solution is measured in a glass cell of length 1 cm., the volume of which is of no importance since all cells are chosen to be of such dimensions as to cover the light path completely. It must be realised, however, that since the concentration of the solution in this cell must remain constant, glass cells must be perfectly clean and dry or previously rinsed out with the solution under test.

In the actual calibration 10 successive weights each of 0·5 grm. of an " H.H.P." iron or spectroscopically pure iron are dissolved and to these known volumes of a standard permanganate solution added. The volumes taken are 1, 2, 3 up to 10 ml., representing 0·00025, 0·0005, 0·00075 up to 0·0025 grm. of manganese, *i.e.* 0·05, 0·10, 0·15 up to 0·50 per cent. manganese in a sample of weight 0·5 grm. Thus

10 artificially prepared steel solutions containing known percentages of manganese have been obtained and their absorptions measured as for the actual determination.

The drum readings are plotted on the ordinate and the percentage of manganese on the abscissa—hence the calibration graph results. It is advisable that on all calibration graphs the scale used should be of such a type that 0·1 drum division is represented by at least one inch, and the percentage of the element present is on a commensurate scale.

Referring again to the method of obtaining the calibration of manganese in ferrous alloys, ten points will be obtained, and these should form a perfectly smooth curve as shown in Fig. 7 for 1 cm. cells. Should any points deviate from this smooth curve, two or three further readings in this vicinity should be obtained.

It has been found, as the result of no little experience on routine analyses, that there is a tendency when constantly referring to calibration graphs that time is wasted and errors inevitably occur. In order to avoid this, it has been found advisable, once the calibration is fixed, to obtain a table of figures from the graph, such that for every 0·01 drum division between 0 and 1·00/1·30 there is a corresponding figure for percentage element. Such tables can be filed in a loose-leaf binder, which can be housed in the Absorptiometer cabinet for easy reference. Fig. 7 shows the calibration graphs for manganese in ferrous alloys using the tungsten lamp, and the corresponding table of figures for the 1 cm. size of cell is given in Table IV.

TABLE IV—**Conversion Table taken from a Calibration Graph**

Materials—Steel.
Filters—Spectrum Green No. 604 and Heat Absorbers.
Setting—Water to Water 1·0.

Element—Manganese (*Range* 0–0·5%).
Cell Size—1 cm.
Light Source—Tungsten lamp.
Method—Difference.

Drum Readings.	0	1	2	3	4	5	6	7	8	9	Mean difference for drum readings 0·005.
0·00	·000	·005	·010	·016	·021	·026	·031	·036	·042	·047	·003
0·10	·052	·057	·063	·068	·073	·079	·084	·089	·094	·100	·003
0·20	·105	·111	·116	·122	·127	·133	·138	·144	·149	·155	·003
0·30	·160	·166	·171	·177	·182	·188	·193	·199	·204	·210	·003
0·40	·215	·220	·226	·232	·238	·243	·249	·255	·260	·266	·003
0·50	·272	·277	·283	·288	·294	·300	·305	·311	·316	·322	·003
0·60	·328	·334	·340	·346	·352	·358	·363	·369	·375	·381	·003
0·70	·387	·393	·398	·404	·410	·416	·422	·427	·433	·439	·003
0·80	·445	·451	·457	·463	·469	·475	·481	·487	·493	·499	·003
0·90	·505	—	—	—	—	—	—	—	—	—	—

When using the mercury lamp, the chemical procedure as outlined previously is followed, with the single exception that it is generally found unnecessary to take blank readings. Typical calibration graphs for manganese in ferrous alloys are shown in Fig. 8, using 0·5, 1·0, and 2·0 cm. cells, and the filters detailed under this determination in Part II. It will be seen that using this type of lamp, direct drum readings are taken and a straight line nearly always results for the calibration graphs. Such graphs are of a different type from those obtained with the tungsten lamp, the former crossing the ordinate at a position closely approximating to the water setting used for the particular determination and the latter approximately through the origin.

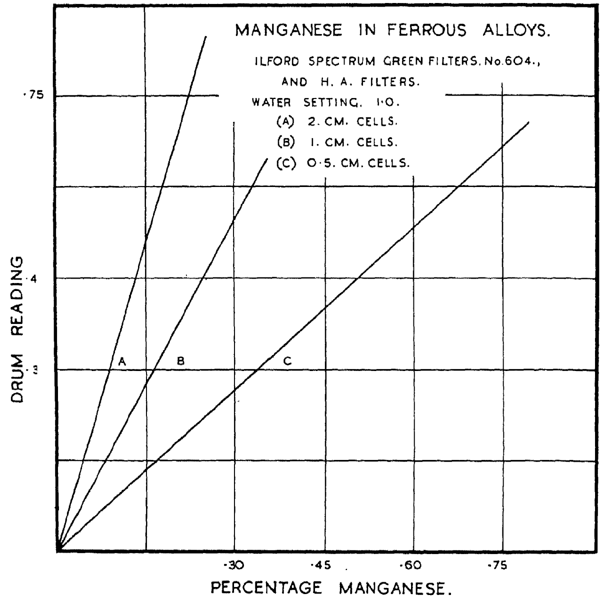


FIG. 7. Calibration graphs for **MANGANESE** in ferrous alloys, using the Tungsten Lamp.

The reason for the deviation of such graphs from the exact water setting and from zero needs a little explanation. In the case of the tungsten lamp, more often than not the graph does pass through the origin; when it does not, this is due to a trace of colour produced by substances other than the specific colour-producing reagent and absent from the blank solution.

In the use of the mercury lamp, as has been explained previously, no blank solutions are taken and in some cases the calibration graph does cross the ordinate at the prescribed water setting. When it does not, this is due to a slight light absorption by the major constituent of the alloy under examination.

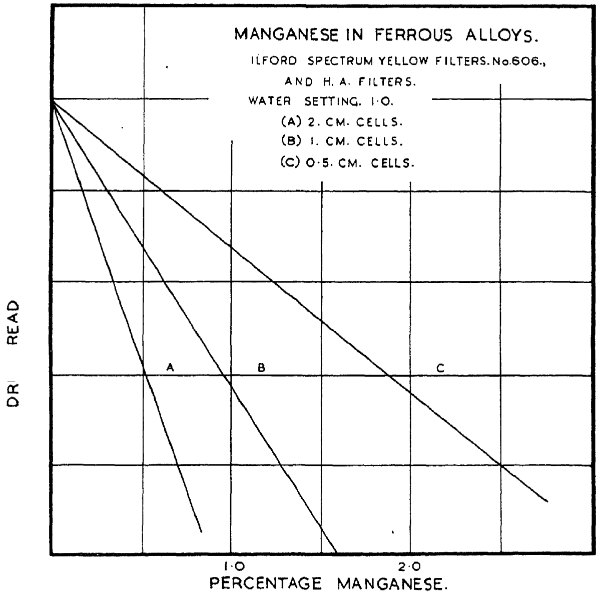


FIG. 8. Calibration graphs for **MANGANESE** in ferrous alloys, using the Mercury Lamp.

Correction Graphs

In some determinations the addition of the reagent producing a specific colour for a particular element, reacts with either the major or some other element always present in the alloy to produce a slight additional coloration. This latter colour is directly proportional to the amount of the interfering element present, and in order to allow or correct for this a further graph, termed a correction graph, is necessary. This is prepared in exactly the same manner as a normal calibration graph, except that definite amounts of the interfering element are employed instead of the element being determined. It is, of course, necessary to know the percentage of the interfering element present. The drum reading due to the absorption of the known percentage of this interfering element is then read off from the correction graph and this reading deducted from the total drum reading obtained. Thus the percentage of the element being determined is obtained. The following example illustrates the use of the correction graph :—

In the determination of iron in copper alloys the iron is coloured up by the thiocyanate reaction. Under the conditions of this method green cupric thiocyanate is also formed and this produces interference and a correction must be applied. A 70/30 brass was analysed by this method for iron ; using a tungsten lamp the drum difference reading obtained was 0·45—this, without applying the copper correction figure, was equal to 0·89 per cent. iron. Applying the copper correction graph a drum reading of 0·07 was obtained for 70 per cent. copper ; hence the actual drum reading due to iron alone was $0{\cdot}45-0{\cdot}07=0{\cdot}38$; this latter figure being equal to 0·75 per cent. iron.

Wherever a correction graph is necessary, the full details are given under the appropriate determination in Part II.

The general practical considerations which appertain to a specific determination apply more so to the corresponding calibration. Thus as the calibration graph, or the corresponding table derived therefrom, is used for many thousands of determinations it should be carried out under the very strictest possible conditions. In order that the main factors governing the production, stability, and reproducibility of the results shall be maintained subsequent to calibration, it is necessary to observe the following points :—

(*a*) *Time and temperature.* In some determinations the time and temperature of development of colour is somewhat critical, for example, the determination of aluminium in magnesium alloys. It is therefore necessary in order to obtain consistency that the calibration graph should be produced under average conditions of time and temperature.

(*b*) *Cleanliness of glass cells.* Although scrupulous cleanliness of all parts of the instrument has been mentioned earlier, it cannot be too strongly emphasised that particular care should be given to the glass cells, and reference should be made to the notes given on page 27 under "glass cells."

(*c*) *Calibrated glassware.* Whilst it is obvious that the use of accurately calibrated glassware, such as volumetric flasks, pipettes, and burettes, is an essential for accurate determinations, it is advisable, if possible, to use N.P.L. standardised ware always.

If this is not available, then the same glass ware as is employed for the calibration should be used.

(*d*) *Blanks for chemical reagents.* Practically all determinations are carried out on extremely small amounts of material and thus the presence, from external sources, of small amounts of the element undergoing examination will influence the final result. This demands that all the reagents used shall be of the highest purity obtainable. Even with these precautions, however, interference may be caused in a determination by impurity in reagents and pick-ups from the apparatus used. In the determination of phosphorus in phosphor-bronze the weight of phosphorus present in the cell when the final measurement is made is of the order of 5×10^{-6} grm. It is therefore imperative in such cases to carry out a blank determination with the reagents used. Except in a few exceptional cases which are specifically mentioned in Part II (viz., cobalt in ferrous alloys, aluminium in magnesium alloys, and certain determinations using the mercury lamp) the calibration curve should pass through the origin. If it does not the purity of the reagents used must be questioned.

(*e*) *Variation in the characteristics of certain organic reagents.* Organic reagents obtained from different sources have been found in some cases to give slightly varying characteristics in the colour produced, both in intensity and tint. All fresh supplies obtained subsequent to calibration should therefore be checked to see if recalibration is necessary.

Use of Glass Cells

The glass cells for containing the solutions under test are made in several sizes, and may be selected for use according to the intensity of light sensitivity of any given solution. They are of the rectangular type, extremely durable and robust, being made of glass and of fused construction. Thus they are completely unattacked by acids normally used in the laboratory, and for chemical resistance may be compared with a flask or beaker. Each cell is annealed to relieve all stresses. Furthermore, the length of each cell is guaranteed to within ±0·5 per cent.

The normal sizes used are listed below, together with their nominal volumes :—

Length of Cell	0·5 cm.	1·0 cm.	2·0 cm.	4·0 cm.
Volume of Cell	4·9 ml.	7·7 ml.	14·7 ml.	31·0 ml.

A more elaborate type is the flow-through cell, which is eminently suitable for routine work. A funnel is arranged in the top and an outlet at the bottom which may be connected to a drainage supply.

Upon the cleanliness of the glass cells depends to a large extent the accuracy with which readings may be taken. All glass cells should be placed in an acid bath for pickling when not in use ; if the cells are cleaned in the same room in which the instrument is kept, a chromic-sulphuric acid mixture is suitable, whilst elsewhere the more volatile hydrochloric acid may be used. It is advisable never to lay the cells in the pickling dish except with one ground glass face downwards. After pickling, the cells should be thoroughly washed and rinsed, inside and out, with distilled water. They may conveniently be allowed to dry on a pad of blotting paper or filter paper. Before use, any moisture should be wiped off with a soft cloth and the surfaces polished. When moving the cells from one place to another, it is convenient to place them in one of the wooden racks provided for the purpose. A convenient layout is shown in Fig. 4.

CHAPTER IV

DISCUSSION AND GENERAL NOTES

Advantage of Absorptiometric Methods over other Methods

In the foregoing notes attention has been drawn to the limitations of the older colorimetric methods of analysis and the manner in which these have been overcome by the use of photo-electric methods. In recent years the increasing use of physical methods to assist chemical analysis has brought about the development of an instrument producing results with an accuracy equal to that of the best gravimetric and volumetric methods. At the same time the range of determinations is increasing rapidly and is no longer confined to the narrow limits of trace elements.

Using the Spekker Photo-electric Absorptiometer a number of advantages are to be gained over other similar instruments, by reason of the fact that a compensating photocell is balanced against an indicating photocell. Thus the effect of variations in the mains supply, which cause a variation in the incident light intensity, is obviated. Other obvious advantages may be summarised briefly as follows:—No batteries required; few optical surfaces to be kept clean; complete independence of the visual judgment of the observer and of the use of permanent standards.

The physical advantages inherent in the Absorptiometer have led to the development of a practically new technique in metallurgical analysis. This is due largely to the early work of Vaughan and his collaborators, who showed that many of the time-consuming factors in gravimetric and volumetric analysis, such as filtration, precipitation, drying to constant weight, and evaporations could be obviated. More important still, the inaccuracies which were inherent in these operations are automatically eliminated. Furthermore, the methods evolved, many of which are given in detail in Part II, whilst being rapid and accurate, result in a very considerable saving in the chemicals employed.

What may have seemed a desirable goal to many metallurgical chemists in the past, that of successfully analysing for a number of elements from a single weighing, has been realised by the use of this technique. Such combined methods termed composite schemes of analysis are now in use for most of the well-known standard engineering alloys, and it is significant to note that new methods recently published fit into such schemes admirably. Thus by reference to Fig. 18, Part II, which gives the composite scheme of analysis for ferrous alloys, it will be seen that by taking only the one weight of alloy, namely 2 grm., seven elements, manganese, chromium, vanadium, copper, cobalt, nickel, and molybdenum, may be determined with a precision equal to and a speed surpassing that of the older methods. Another significant point is that generally speaking the new absorptiometric method is suitable for the determination of a particular element in any class of alloy in the same category. Thus, the method used for the determination of manganese, in a straight carbon steel, applies equally well to the determination of the same element in an austenitic steel, a tool steel, a high speed steel, and an alloy cast-iron. These methods have been evolved within the last three to four years, and it is probable that in the future more elements may be added to this list. What has been mentioned concerning ferrous alloys is just as applicable to copper, aluminium, and magnesium alloys.

Limitations of Absorptiometric Methods of Analysis

Where Absorptiometric methods of analysis tend to compare unfavourably with gravimetric and volumetric methods of metallurgical analysis, is in the final measurement taken, which is related to a limiting concentration of the element concerned. This is a limitation inherent in all photometric methods and is very apparent when the colour of a solution is measured visually, the colour being so dense that dilution is essential.

In the case of the Absorptiometer, the dilution method may be employed, but in certain cases the absorption of the coloured solution may be seriously affected by dilution, *e.g.* the determination of silicon in ferrous and non-ferrous alloys. In some other determinations, *e.g.* aluminium in magnesium alloys, the amount of reacting reagent added is, for various reasons, limited, and only a slight excess beyond that called for by the stoichiometric equation is used.

However, methods are available for increasing or decreasing the concentration of a solution that can be measured, as follows :—

(*a*) Use of different sizes of cell.
(*b*) Adjustment of initial weight of alloy taken.
(*c*) Dilution of the final coloured solution.
(*d*) Use of various colour filters.
(*e*) Use of various water settings.

(*a*) From Beer's and Lambert's law, previously stated in Chapter I, it can be shown that with two solutions of the same element—in solution under the same conditions—of concentrations C_1 and C_2 respectively and contained in cells of lengths l_1 and l_2 respectively, that when the two solutions show the same light absorption then :—

i.e. under the conditions mentioned, the concentration is inversely proportional to the lengths of the absorbing layer of the solution. Thus it follows from this relationship that with a solution which is too concentrated to give a reading of any accuracy on the instrument using, say, a 2 cm. cell, then a smaller size of cell should be used until the absorption is measurable with accuracy. Thus the absorption of the solution may be reduced to measurable dimensions by using 1·0 and 0·5 cm. or even 0·25 cm. cells. By such a means the light absorption is roughly one-half, one-quarter, or one-eighth respectively of that when employing a 2 cm. cell.

It cannot be too strongly emphasised, however, that where it is necessary to employ more than one size of glass cell, it is essential to prepare a separate calibration graph for each size. The graphs so prepared are usually of the same shape when using the tungsten lamp—and nearly always pass through the origin—and for the mercury vapour lamp are straight lines which nearly always cross the ordinate at the predetermined water setting. It is obvious that the graphs in either case are not coincidental. For all those solutions which obey Beer's law, if a series of calibration graphs are prepared using 2, 1, and 0·5 cm. cells and these are plotted on the same graph, the ordinate being used for drum readings and the abscissa for concentration and percentage of the element present, then the graphs obtained usually take the form and relative positions shown in Figs. 7 and 8.

This method of plotting the graphs is not generally adopted in practice, as by doing so the essential accuracy is lost. It is customary to use the abscissa so that it is employed to best advantage, relative to each size of cell employed. This may be illustrated from Fig. 7, showing the calibration graphs for manganese in steel using the tungsten lamp and 2, 1, and 0·5 cm. cells. The ranges of manganese concentration given by the various cells are as follows :—

Cell size	2·0 cm.	1·0 cm.	0·5 cm.
Mn. %	0–0·25%	0–0·50%	0–1·0%

Consequently, the final calibration graphs will have the abscissa divided over the whole of their length to cope with the appropriate cell size and concentrations as given above. Graphs plotted out in this manner are more useful for routine work ; they are not coincidental.

(*b*) Obviously by altering the initial weight of an alloy taken for a determination, the concentration of the element to be determined is altered proportionately. Another way in which this may be effected is by taking a standard weight and diluting after the solution of the alloy is obtained.

(*c*) If a coloured solution is finally obtained for a specific determination and it is found that the absorption cannot be measured accurately, even when using different sizes of cell, then dilution of the coloured solution may be used, the same dilution affecting the blank solution. There are, however, exceptions to this method, which are listed in Table V.

(*d*) Different colour filters may be used to give a higher or lower absorption for a given concentration of element, but the method is somewhat lengthy, as a separate calibration is required for each colour filter and also, owing to the blank readings obtained with some methods, the colour filters have to be chosen with discretion.

(*e*) Slight increase of the water setting up to, say, a drum reading of 1·3 may be made to increase the concentration that can be measured, provided the sensitivity then obtainable is suitable for the accuracy required.

The table on the following page summarises what factors may or may not be altered in order to obtain a suitable absorption reading.

Accuracy and Factors affecting Accuracy

Some discussion has already taken place regarding accuracy, but the general limit to be expected using the Absorptiometer under ideal conditions is ±1 per cent. of the concentration of the element present when the whole workable range of the drum is utilised. The actual limits obtained are given under each determination in Part II. As in all analyses the accuracy is affected by the final measurements taken, and in this case it is that of the drum reading. It has been mentioned in Chapter III that the drum is calibrated between 0 and 0·6 in steps of 0·01, and between 0·6 and 1·3 in steps of 0·02; nevertheless the highest accuracy with which measurements may be taken is 0·005 between both the ranges mentioned.

The accuracy of measurement made by the Absorptiometer may be determined by (*a*) limitations of chemical analysis, or (*b*) properties of the Absorptiometer. When the limit of accuracy is set by the instrument, it is found that errors amount to about 0·5 per cent. of the actual concentration to be determined, if the instrument is used in accordance with the instructions for use supplied with it, and with the most suitable cell length and concentration of solution.

The theory of photo-electric instruments of this type (Twyman and Lothian, *Proc. Phys. Soc.*, 45, 643, 1943) shows that the greatest accuracy should be obtained by using a solution of density about 0·43. In actual practice, however, in the case of the Absorptiometer the accuracy is limited by the degree of stability of the photocell, a factor

TABLE V—**Methods Available for Dilution**

Determination.	Methods of effecting dilution.		
	Different Sizes of Cell.	Adjustment of Initial Weight.	Dilution of Final Solution.
		Ferrous Alloys	
Manganese	Yes	Yes	Yes
Chromium	Yes	Yes	No—maintain acid concentration
Vanadium	Yes	Yes	Yes
Copper	Yes	Yes	No
Cobalt	Yes	Yes	No
Nickel	Yes	Yes	No
Molybdenum	Yes	Yes — if iron concentration is maintained	No
Silicon	Yes	Yes	No
Titanium	Yes	Yes	Yes
		Copper Alloys	
Copper	No	Yes	No
Manganese	Yes	Yes	Yes
Iron	Yes	Yes — with provisos	No
Phosphorus	Yes	Yes	No
Nickel	Yes	No	No
		Aluminium Alloys	
Manganese	Yes	Yes	Yes
Copper	Yes	Yes	No
Iron	Yes	Yes	No
Nickel	Yes	Yes	Yes
Silicon	Yes	Yes	No
Titanium	Yes	Yes	Yes
		Magnesium Alloys	
Aluminium	Yes	Yes — with provisos	No
Manganese	Yes	Yes	Yes
Copper	Yes	Yes	No
Iron	Yes	Yes	No
Silicon	Yes	Yes	No

which is not taken into account in the above-mentioned theory. Actually, it is found that the greatest accuracy is obtained by using solutions of density between 0·6 and 1·0.

Little further stress need be laid upon other factors affecting accuracy, such as initial weights and measurement of volumes, as these are obvious using any quantitative method of analysis ; but it may be taken as axiomatic that unless the instrument is properly manipulated and scrupulously clean, erroneous figures will result.

A further factor not connected with the operative side of the equipment is that of the limiting concentration of the particular element being determined in the alloy. Average errors of ±1 per cent. have been cited, and whilst this figure provides results comparable with and in many cases better than standard methods over the particular ranges of elements cited in Part II, it should be realised that when working *above* the limit of this range, the accuracy in terms of absolute content will tend to fall off ; and when working *below* the limit, although the same accuracy of absolute content may be maintained, the accuracy as a percentage of the absolute content will fall off. Thus, although it is possible to carry out a very rapid determination of titanium in ferro-titanium with a titanium content of 30 per cent., the error is of the order of ±0·3 per cent. titanium, which in some cases is not within desired limits.

Summing up, it may be said that the accuracy obtainable with the Absorptiometer is superior to that obtained using other physical instruments, such as the spectrograph and the polarograph.

Time taken for one determination

This figure, representing one of the chief advantages of the Absorptiometer, is cited for each determination in Part II ; but it should be noted that the figure given, whilst truly representative of results obtained in practice, is the average time for one analysis when a number of determinations are performed on a batch of similar samples.

Suggested Apparatus for Absorptiometric Analysis

No highly specialised equipment, apart from the Absorptiometer and its ancillary equipment, is required for metallurgical analysis, and the following are merely suggestions based upon practical experience from users of the instrument in industry. It will be realised that the suggestions by no means cover every requirement and are given merely as a guide to future users :—

Glass Beakers—Conical type, size 650, 400, and 250 ml. capacity ; Squat type, sizes 250 and 100 ml. capacity.

Nickel and Silver Beakers—150 ml. capacity.

Burettes—N.P.L.(A) type, 50 and 25 ml. capacity.

Pipettes—High grade 50, 25, 20, 10, and 5 ml. single mark type; 25 and 10 ml. calibrated type.
Automatic pipettes of sizes as quoted above.

Aspirators—5 litre to 500 ml. type—coupled up to automatic pipettes.

Volumetric Flasks—High grade 2 litre, 1 litre, 500, 250, 200, 100, and 50 ml. capacity.

Graduated Cylinders—250, 100, 50, 25, and 10 ml. capacity.

Dropping Bottles—100 and 50 ml. capacity.

Chemicals—Generally of A.R. quality throughout — for precise details see determinations given in Part II.

Standard Alloys—A number of pure metals and standard alloys are useful for calibration and checking up, and the specific requirements are given in Part II.

Possible future developments

It will be appreciated from what has been given so far in this book that the study of absorptiometric methods of metallurgical analysis is only in its infancy. The older colorimetric reactions have been adapted to provide methods suitable for the high standard required in metallurgical analysis. At the same time, newer reactions, mostly with organic reagents, have been developed and applied. There is no doubt that the future development of the Absorptiometer will be greatly enhanced by work in this field, when more is known of the precise reactions between metals and complex organic radicals.

Almost untouched fields, as far as metallurgical analysis is concerned, are those of turbidimetry, nephelometry, and fluorimetry. There are definite possibilities in such directions, but at present it remains to be seen whether these possibilities can be realised in industry. It is possible, for example, that the analysis of zinc in aluminium or magnesium alloys may be effected by using the reaction of zinc with potassium ferrocyanide. The use of special colour filters might be employed in this reaction to prevent the absorption of interfering colours in the solution. Another possible development lies in the use of indirect reactions, in order to determine elements which at present cannot be analysed by the usual direct reaction between the metal ions and a given radical to produce a specific coloured solution. Such an example is that of tin in brasses and bronzes, where the tin might be converted to stannous chloride and this reducing agent determined by a suitable method. Another example is the application of the decolorising of a coloured solution, by a compound of the particular element to be determined—such as the conversion of sulphur to sulphur dioxide and the latter reducing a solution of potassium permanganate.

The possible future developments so far envisaged have been largely on the chemical side and as applied to the Absorptiometer in its present form, but without doubt it is to the physical side that we must look for an enlargement of the scope of absorptiometric analysis. Early workers used the tungsten lamp in conjunction with selective colour filters. These, although providing restricted spectral bands, were still of width 500–700 A. Greater light selectivity was achieved with the mercury lamp emitting some five main spectrum bands of narrow width which, with the use of colour filters, could be selected at will. Such is the present position to-day, and it must be obvious that since light selectivity is probably the most important factor in absorptiometry, the use of a monochromator, or other means of providing a definite spectrum line at will, over any part of the spectrum, is essential for the full development of the method. It is more than likely that using a monochromator the response of the present photocells will be weak, calling for amplification by means of valve circuits, in order that the response may be measurable. On the other hand improvements in photocells and methods of measuring the absorption are more a matter of evolution in practice and experience. Thus, in the very near future it may be possible, by the use of a monochromator, to determine vanadium, titanium, and molybdenum in the same steel solution, merely by the reaction of their salts, all of which form yellow solutions with hydrogen peroxide.

As mentioned in Chapter II, it is essential when using the Absorptiometer for metallurgical analysis to use, what is now standard for such work, a mirror "Spot" galvanometer. Such instruments are much more sensitive than the needle type. Perhaps in the future electrical means other than galvanometers may be used of greater robustness and sensitivity, to indicate the photocell response.

The Literature of Absorptiometric Metallurgical Analysis

The following list is not intended to be exhaustive ; it gives publications which may act purely as a guide to the study of absorptiometry, as applied to metallurgical analysis :—

(1) E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by The Institute of Chemistry, 1941.

(2) E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer for Metallurgical Analysis.* Monograph published by The Institute of Chemistry, 1942.

(3) J. H. Yoe. *Photometric Chemical Analysis*—Vol. I. *Colorimetry*, Vol. II. *Nephelometry*. J. Wiley ; Chapman and Hall, 1928-29.

(4) E. D. Snell and C. R. Snell. *Colorimetric Methods of Analysis*—Vol. I. *Inorganic*. Van Nostrand ; Chapman and Hall, 1936.

(5) *Absolutkolorimetrische Metallanalysen mit dem Pulfrich-Photometer*. Carl Zeiss, Jena, 1938.

(6) *Analysis of Aluminium and its Alloys*. The British Aluminium Co., Ltd., 1941.

(7) *Organic Reagents for Metals*. Hopkins and Williams, London, 1943.

(8) *The B.D.H. Book of Organic Reagents*. The British Drug Houses, London, 1941.

(9) F. Feigl and J. W. Matthews. *Qualitative Analysis by Spot Tests*. Nordemann Publishing Co., 1937.

(10) I. Mellan. *Organic Reagents in Inorganic Analysis*. The Blakiston Co., Philadelphia, 1941.

(11) F. Twyman and C. B. Allsopp. *The Practice of Absorption Spectrophotometry*. A. Hilger, Ltd., 1941.

Conclusions

An attempt has been made to give the essential details underlying the manipulation of the Absorptiometer as applied specifically to metallurgical analysis, together with most of the details known for the determination of many of the elements in standard engineering ferrous and non-ferrous alloys. In connection with the latter—collected together in Part II—only those methods which have proved their value in industry are included. It is to be noted that probably other methods are in use and Part II must not be regarded as complete and conclusive. It is hoped that the subject matter and determinations have been presented in such a manner as to be of real use to the practical metallurgical chemist.

PART II

SOME ABSORPTIOMETRIC METHODS OF ANALYSIS

CHAPTER V

FERROUS ALLOYS

Introduction

THIS section of the book is concerned essentially with practical methods which have been evolved, using the equipment previously described in Part I. Such methods can be conveniently divided into two main groups, which are discussed in detail below.

In colorimetric analyses it is usual to separate out all interfering anions and cations prior to colouring up the element which is being determined or to separate the latter by differential solvent action. The coloured solution or complex of this element is then matched against the same complex made from a solution of known concentration. A different procedure is adopted in absorptiometric analyses using the Absorptiometer. In practically all cases, with rare exceptions, separation of interfering elements is not necessary.

(1) Difference Methods

The alloy in question is taken into solution and from an aliquot portion of this solution the particular element being determined is coloured up in the presence of the other elements. The absorption of this solution is then determined, using filters which are chosen because they are known to give the maximum absorption of light for the colour of the particular complex in question; a similar aliquot is taken and not coloured up and the absorption measured under identical conditions. The difference between the two readings so obtained on the instrument is due solely to the coloured complex of the element sought. This is the basic principle underlying difference methods, although reference to particular methods will show variations of this technique.

It has been found in general metallurgical analyses, as opposed to analyses conducted on a special class of alloys, that, when using the tungsten lamp in the Absorptiometer, difference methods must be applied.

(2) Direct Methods

When determinations of certain elements are confined to a particular class or range of alloys, either ferrous or non-ferrous, it is possible using a tungsten light source to apply direct methods. In such cases the absorption reading due to interfering elements is for all practical purposes the same, and having once determined this figure it remains a constant for subsequent analyses.

As has been explained in Part I, the mercury vapour lamp employs the principle of selective absorption of the coloured complex of the element to be determined ; hence only one reading is required in most cases.

Full analytical procedures for ferrous and non-ferrous alloys which have been developed using the Absorptiometer are given. In general the chemical procedures are entirely similar whether the tungsten or mercury vapour lamp is used, the main difference being that special filters are used with the latter. In consequence the information concerning analytical procedures using both types of lamp is given under the one determination.

These methods are sub-divided under four main headings as :—

(1) Ferrous alloys—cast irons and steels.
(2) Copper alloys—brasses, bronzes, and the like.
(3) Aluminium alloys.
(4) Magnesium alloys.

Ferrous Alloys

The determinations given are for the following elements in steel and cast iron :—Chromium, Cobalt, Copper, Manganese, Molybdenum, Nickel, Silicon, Titanium, and Vanadium.

In every method given it is advisable to use, throughout, reagents of the best analytical quality procurable.

It will be noted that the opening out for most alloys is with spekker acid—a sulphuric-phosphoric acid mixture (see page 44)—and this has been found suitable for most steels encountered in industry. In the case of straight and alloyed cast irons, it is only necessary to filter off the graphite after the oxidation stage with nitric acid.

It is probable that with highly alloyed steels complete solution cannot easily be effected with spekker acid. In such cases *aqua regia* may be employed and when solution is complete spekker acid added. Care must be taken to remove all hydrochloric acid by subsequent heating to fumes of sulphur trioxide.

In the case of carbides remaining undissolved—chiefly carbides of chromium and molybdenum as encountered with high speed steels—it is essential to heat the solution to fumes of sulphur trioxide.

Determination of Chromium in Ferrous Alloys

(0–0·25 per cent. Chromium)

(B) DIRECT METHOD

(1) Tungsten Lamp

No difference method is necessary with the procedure outlined below.

This method is applicable to the determination of chromium in steels and cast irons over the range 0–0·25 per cent. chromium.

The alloy is dissolved in a sulphuric-nitric acid mixture, the iron precipitated and the chromium oxidised to chromic acid by the addition of caustic soda and sodium peroxide. Dichromic acid is coloured up in acid solution by means of diphenylcarbazide.

REAGENTS REQUIRED

Sulphuric acid . . .	25 per cent. solution.
Nitric acid	S.G. 1·42.
Potassium permanganate	3 per cent. solution.
Caustic soda	25 per cent. solution.
Sodium peroxide . . .	Solid.
Diphenylcarbazide . .	Take 1 grm. of diphenylcarbazide, dissolve in about 75 ml. of alcohol, add 6 drops of sulphuric acid (S.G. 1·84) and make up to 100 ml. with alcohol.
Potassium dichromate .	Solution standardised to contain 0·1250 grm. of chromium per litre.

METHOD

Take 0·5 grm. of the alloy in a 400 ml. conical beaker and add 10 ml. of sulphuric acid and 5 ml. of nitric acid. Simmer to dissolve and when the reaction ceases dilute with 100 ml. of hot distilled water and add potassium permanganate solution dropwise until the solution is permanently pink. Boil for 5 mins. and add 30 ml. of 25 per cent. caustic soda solution, 1 grm. of sodium peroxide and boil for 10 mins. Cool, dilute to 250 ml. with water and allow to stand until the precipitate settles. Decant sufficient liquid for a 25 ml. fraction through a sintered glass funnel and take 25 ml. of the filtrate in a 250 ml. conical beaker. Add 4 ml. of 25 per cent. sulphuric acid, cool, and add 2 ml. of diphenylcarbazide solution. Dilute to 50 ml. with water and measure off the absorption of this solution using Ilford Spectrum Green filters No. 604, 1 cm. cells and a water setting of 1·0.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised potassium dichromate solution and treat exactly as given under method. Plot the relationship between drum readings and percentage of chromium.

There is no need to calibrate other than with 1 cm. cells covering the range 0–0·25 per cent. chromium.

A typical calibration graph, obtained by using 1 cm. cells, is given in Fig. 9.

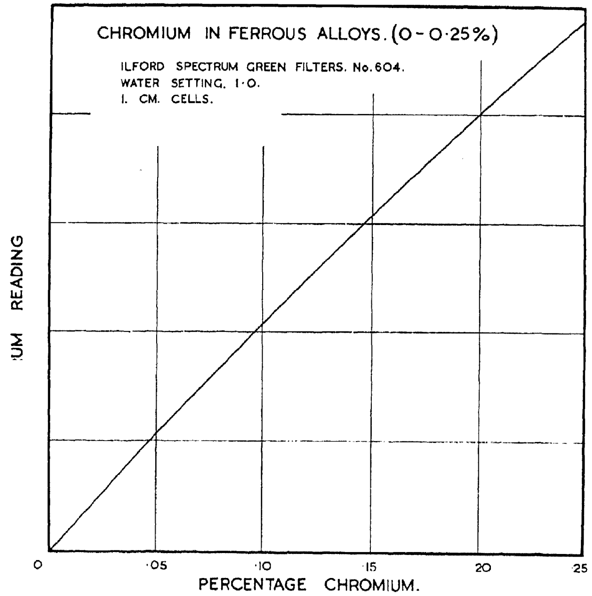


FIG. 9. Calibration graph for **CHROMIUM** in ferrous alloys.

NOTES AND HINTS

(1) To prevent bumping during the boiling of the solution and precipitate, broken porcelain should be used.

(2) When using a new batch of diphenylcarbazide it is advisable to check up on the calibration. In view of this, it is suggested that a relatively large stock should be obtained initially.

(3) Although vanadium and molybdenum produce colorations with diphenylcarbazide, under the conditions set out in the method,

these do not interfere in the amounts likely to be present in such alloys.

(4) A slight blank will be obtained from the diphenylcarbazide reagent when calibrating, and this should be checked from time to time as follows:—Add 2 ml. of 5 per cent. sulphuric acid to 2 ml. of 1 per cent. alcoholic diphenylcarbazide solution and make up to 50 ml. with water. Measure off the absorption under the standard conditions given.

LIMITS OF ACCURACY

This method gives an accuracy of ± 2 per cent. of the chromium content of the ferrous alloy.

TIME FOR ONE DETERMINATION

About 15 to 20 minutes when done in batches.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, pp. 17, 18.

Determination of Chromium in Ferrous Alloys

(0·2–12 per cent. Chromium)

(A) DIFFERENCE METHOD

Tungsten Lamp

The information given herewith applies to the determination of chromium in steels and cast irons over the range of 0·2–12 per cent. of chromium.

The alloy is dissolved in a sulphuric-phosphoric acid mixture and is oxidised as for manganese by the silver persulphate reaction. The manganese is oxidised to permanganic acid and the chromium to dichromic acid; by the addition of sodium nitrite solution the former is decolorised without affecting the latter.

Difference readings are taken which are proportional to the percentage of chromium in the steel or cast iron.

REAGENTS REQUIRED

Spekker acid	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid . . .	S.G. 1·20.
Silver nitrate . . .	2 per cent. solution.
Ammonium persulphate	2·5 grm. solid or " Analoids."
Urea	0·5 grm. solid or " Analoids."
Sodium nitrite . .	2 per cent. solution.
Potassium dichromate	Solution standardised to contain 6·000 grm. of chromium per litre.
Sulphurous acid . .	Saturated solution.

METHOD

Take 1·0 grm. of the steel in a 250 ml. beaker and add 40 ml. of spekker acid. Simmer to dissolve and when the reaction ceases add 5 ml. of nitric acid. If carbides remain undissolved continue boiling until fumes of sulphur trioxide appear. Cool and make up to 100 ml. with water. Take two 50 ml. aliquots and treat as follows :—

(1) *Blank Solution*--Make the 50 ml. aliquot up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of 2 per cent. silver nitrate solution and 2·5 grm. of ammonium persulphate. Boil until the evolution of oxygen is complete and cool. Add 0·5 grm. of urea and make up to 100 ml. with water. Rinse out a 1 cm. glass cell with this solution, add 1 drop of sodium nitrite solution to the cell and fill up with the solution.

Measure the absorption of (1) and (2) employing Ilford Spectrum Violet filters No. 601 and a water setting of 1·0. The difference between these two readings is proportional to the percentage of chromium in the alloy.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised potassium dichromate solution and add 40 ml. of spekker acid to each. Reduce the dichromate with a slight excess of sulphurous acid, boil off the excess sulphur dioxide, cool, and make up to 100 ml. with water. Take two 50 ml. aliquots and proceed exactly as given under method for the blank and colour solutions. Plot a graph showing these difference readings against the percentage of chromium.

The complete range of cells is calibrated as follows :-

Range.	Size of Cell.	Ml. of $K_2Cr_2O_7$ used.	$NaNO_2$ solution used.
0–12% Cr.	0·5 cm.	0, 2, 4, 6 up to 20.	1 drop to each cell.
0–6% Cr.	1·0 cm.	0, 1, 2, 3 up to 10.	1 drop to each cell.
0–3% Cr.	2·0 cm.	0, 0·5, 1·0, 1·5 up to 5.	2 drops to each cell.
0–1·5% Cr.	4·0 cm.	0, 0·25, 0·5 up to 2·5.	4 drops to each cell.

A typical calibration graph is given in Fig. 10 showing the range 0–3% Cr. using 2 cm. cells.

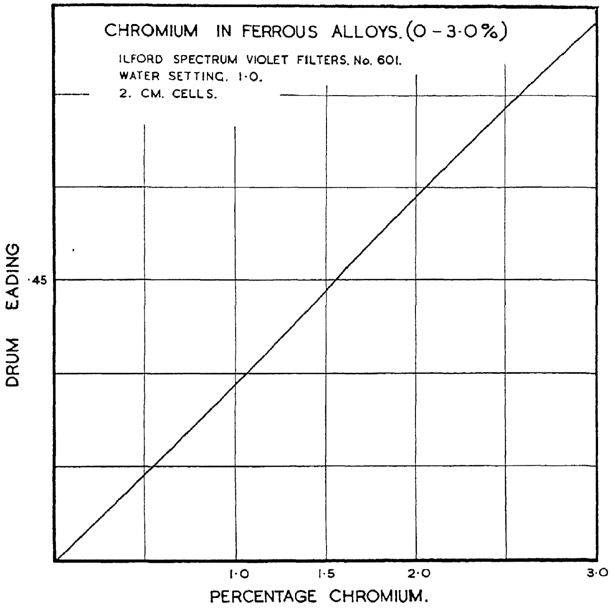


FIG. 10. Calibration graph for **CHROMIUM** in ferrous alloys.

NOTES AND HINTS

(1) When determining chromium in high chromium steels it may be necessary to add more than 2·5 grm. of ammonium persulphate.

(2) When reducing the permanganic acid with sodium nitrite, the urea reacts with the latter to produce small bubbles of nitrogen which, if the cells are not scrupulously clean, adhere to the sides

of the cell and give inaccurate readings. The cure for this is perfectly clean cells.

(3) When working on the range 0–1·5 per cent. chromium it is advisable in the calibration to take, say, 50 ml. of the standardised potassium dichromate solution, make up to 200 ml. with water and then take 0, 1, 2, 3 up to 10 ml. of this solution.

LIMITS OF ACCURACY

This method gives an accuracy of 2 per cent. of the chromium content of the ferrous alloy.

TIME FOR ONE DETERMINATION

About 15 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 15.

(B) DIRECT METHODS

(1) Tungsten Lamp

A direct method is not applicable in this case.

(2) Mercury Lamp

The chemical procedure as given under (A) is followed exactly, except that no blank solutions are required and Ilford Spectrum Violet filters No. 601 and a water setting of 1·2 are used. Furthermore, no blank readings are required in the calibration, except that of the iron solution.

The range covered is as follows :—

Range.	Size of Ce
0–15% Cr.	0·5 cm.
0–7·5% Cr.	1·0 cm.
0–3·5% Cr.	2·0 cm.
0–1·75% Cr.	4·0 cm.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Cobalt in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in spekker acid and the cobalt is coloured up by the use of nitroso-R-salt in a buffered solution. Interference from other metals is avoided by subsequent acidification with nitric acid followed by boiling. In the case of high speed steels, the tungsten is held in solution by means of phosphoric acid.

REAGENTS REQUIRED

Spekker acid	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid	(*a*) S.G. 1·42 ; (*b*) S.G. 1·20.
Nitroso-R-salt	1 grm. of the powdered solid is dissolved in 400 ml. of water, warmed if necessary, and made up to 500 ml. with water.
Sodium acetate	500 grm. of the trihydrate are dissolved and made up to 1 litre with water.
Cobalt sulphate	0·4770 grm. of $CoSO_4.7H_2O$ is dissolved and made up to 2 litres with water. This solution should be standardised to contain 0·05 grm. of Co per litre.

METHOD

Take 0·5 grm. of alloy in a 250 ml. conical beaker and dissolve by heating with 20 ml. of spekker acid. Simmer and when the reaction ceases add 5 ml. of nitric acid (S.G. 1·20), continue boiling until fumes of sulphur trioxide appear, cool, and dilute, dissolving any salts which may appear, and make up to 100 ml. with water. Take two 10 ml. aliquots and treat as follows :—

(1) *Blank Solution*—Add 10 ml. of sodium acetate solution, 5 ml. of nitric acid (S.G. 1·42) and boil. Cool, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of nitroso-R-salt solution, 10 ml. of sodium acetate solution and heat to boiling. Add 5 ml. of nitric acid (S.G. 1·42) and continue boiling for not less than one and not more than two minutes. Cool and make up to 100 ml. with water.

Measure off the absorptions of (1) and (2) using 1 cm. glass cells, Ilford Spectrum Blue filters No. 602 and a water setting of 1·2.

The difference readings between (1) and (2) represent the colour due to cobalt in the ferrous alloy and the percentage of this element is read off from the appropriate calibration graph.

RANGES

The method described is for the range 0–1 per cent. cobalt. For higher concentrations of cobalt a suitable dilution or adjustment of the weight of the sample is necessary. When using different size cells the amount of nitroso-R-salt must be altered in the following manner:—

Range.	Size of Cell.	ml. of nitroso-R-salt solution.
0–0·25% Co.	4 cm.	2·5
0–1·0% Co.	1 cm.	10·0
0–2·0% Co.	0·5 cm.	20·0

To illustrate the above, the following example is given. In the case of a steel containing 10% cobalt the sample weight should be 0·1 grm. and 20 ml. of nitroso-R-salt would be added when colouring up. The absorption of this solution is measured off in a 0·5 cm. cell and the percentage cobalt read off from the calibration graph. The figure so obtained should be multiplied by 5 to give the percentage of cobalt in the steel.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised cobalt solution containing 0·05 grm. of cobalt per litre and to each add 2 ml. of spekker acid and colour up as described in (2) above. To obtain a blank reading omit the addition of the nitroso-R-salt and proceed as given in (1) above. Measure off the absorption of these solutions as given previously and plot the respective differences against the concentrations of cobalt.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of cobalt solution required.	ml. of nitroso-R-salt.
0–2% Co.	0·5 cm.	0, 2, 4, 6 up to 20	20
0–1% Co.	1·0 cm.	0, 1, 2, 3 up to 10	10
0–0·25% Co.	4·0 cm.	0, 0·25, 0·5 up to 2·5	2·5

A typical calibration graph is shown in Fig. 11 obtained by using 1 cm. cells.

NOTES AND HINTS

(1) When fuming down, all nitric acid must be eliminated.

(2) The addition of sodium acetate is not critical and may be within 1 ml. either side of the prescribed amount.

(3) Nitroso-R-salt must be added accurately.

(4) The boiling time should be adhered to fairly strictly, especially in the case of steels containing chromium.

(5) Bright sunlight affects the colour of the solution, but the colour is stable in diffused light.

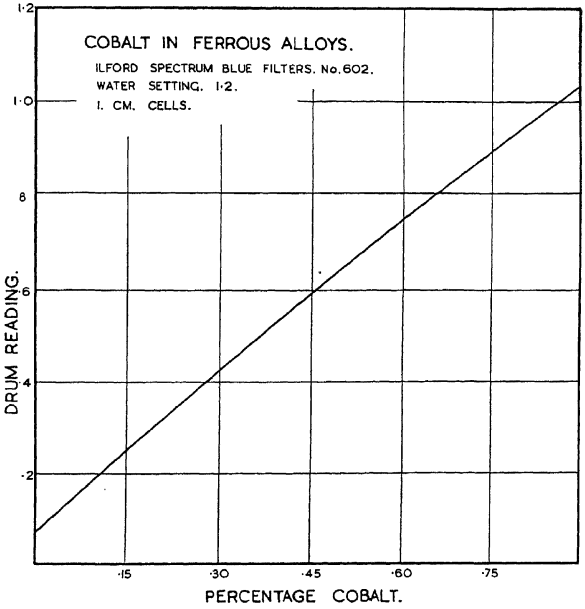


FIG. 11. Calibration graph for **COBALT** in ferrous alloys.

LIMITS OF ACCURACY

Results may be obtained within ±1 per cent. of the average cobalt content of the alloy in question.

TIME FOR ONE DETERMINATION

10 minutes when handled in batches.

REFERENCE

F. W. Haywood and A. A. R. Wood. *Journ. Soc. Chem. Ind.*, March 1943, Vol. XLII, pp. 37–39.

(B) DIRECT METHOD

(1) Tungsten Lamp

The procedure as given under (A) is followed exactly, omitting the use of the blank solution (1).

(2) Mercury Vapour Lamp

The chemical procedure outlined in (A) is followed exactly, omitting the use of the blank solution (1). It is necessary to *use a 0·3 per cent. solution of nitroso-R-salt,* although the volumes for the addition of this reagent remain unaltered. Measure the absorption of the solution using Wratten No. 74 filters and a water setting of 1·2.

The range covered is as follows :—

Range.	Size of Cell
0–3% Co.	0·5 cm.
0–1·5% Co.	1·0 cm.
0–0·75% Co.	2·0 cm.
0–0·35% Co.	4·0 cm.

Determination of Copper in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a sulphuric-phosphoric acid mixture and copper determined in an aliquot portion by the formation of the diethyldithiocarbamate complex in ammoniacal solution. Metals insoluble in ammonia are held in solution by the use of citric acid. Nickel interferes and is removed as the dimethylglyoxime complex.

REAGENTS REQUIRED

Spekker acid . . .	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid	S.G. 1·20.
Ammonium citrate .	500 ml. of ammonium hydroxide (S.G. 0·88) is added to 500 grm. of citric acid until solution is complete and made up to 1 litre with water.

Ammonium hydroxide	200 ml. of ammonium hydroxide (S.G. 0·88) is made up to 1 litre with water—20 per cent. solution.
Ammonium hydroxide	S.G. 0·88.
Colloid	1·0 grm. of gum acacia is dissolved in 100 ml. of hot water and the solution made up to 200 ml. with water.
Sodium diethyldithiocarbamate	0·50 grm. of this reagent is made up to 250 ml. with water.
Dimethylglyoxime	1·0 grm. of this reagent is dissolved in 100 ml. of industrial spirit.
Copper	H.H.P. copper.

METHOD

Copper percentage 0-1% and 0-5%

For alloys containing up to 1 per cent. copper, take 0·5 grm. of the alloy—for higher concentrations of copper take proportionately less quantities—add 20 ml. of spekker acid and heat to dissolve, oxidise with 5 ml. of nitric acid, boil to complete solution and expel nitrous fumes. Fume down, if necessary, to decompose carbides, cool to room temperature and make up to 100 ml. with water. Two slightly different procedures are required, one for alloys containing nickel and one for those without nickel.

(*a*) *Steels not containing nickel*—Take two 10 ml. aliquot portions of the above solution and colour up as follows :—

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide 20 per cent. solution, 10 ml. of gum acacia solution and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide 20 per cent. solution, 10 ml. of gum acacia solution and 40 ml. of water. Shake well, then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up to 100 ml. with water.

Measure the absorption of these solutions on the Absorptiometer by means of 2 cm. cells, Ilford Spectrum Blue filters No. 602 and a water setting of 1·0. The difference between (1) and (2) represents the colour due to copper and is read from the appropriate calibration graph.

(*b*) *Steels containing nickel*—Take two 10 ml. aliquots of the original solution and colour up as follows :—

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide 20 per cent. solution, 10 ml. of gum acacia solution and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide 20 per cent. solution, and 30 ml. of water. Then add 2·5 ml. of dimethylglyoxime for every 5 per cent. of nickel present in the alloy originally and warm at ca. 70° C. for 15 minutes. Add 5 ml. of ammonium hydroxide (S.G. 0·88) and filter through a Whatman's 41 filter paper washing with 20–25 ml. of warm water. Cool the filtrate and add 10 ml. of gum acacia solution, 10 ml. of sodium diethyldithiocarbamate solution, and make up to 100 ml. with water.

Measure the absorption of these solutions as given previously under (*a*).

Copper percentage 0-0·25%

For the determination of copper in ferrous alloys where the copper concentration does not exceed 0·25 per cent. a slightly different procedure is necessitated, and this is carried out briefly as follows :—

The alloy sample of weight 0·5 grm. is dissolved and made up as described for steels containing 0–1 per cent. copper. Take two 20 ml. aliquot portions and colour up as follows :—

(1) *Blank Solution*—Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide 20 per cent. solution, 10 ml. of gum acacia solution and make up to 100 ml. with water.

(2) *Colour Solution*—Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide, 20 per cent. solution, 10 ml. of gum acacia solution and shake well ; then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up to 100 ml. with water.

Measure the absorption of these solutions by means of 4 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The removal of nickel, if present, is carried out as previously described, but adding 5 ml. of dimethylglyoxime solution for every 5 per cent. of nickel present in the alloy.

CALIBRATION GRAPH

(*a*) Copper percentage 0-1% and 0-5%

Take 0·50 grm. of H.H.P. copper and dissolve in 30 ml. of nitric acid (S.G. 1·20), boil to expel nitrous fumes and make up to 1 litre with water. Take 50 ml. of this solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution, and to each volume add 2 ml. of spekker acid and colour up the solution as previously described under (*a*) (2). At the same time carry out a blank determination of the normal reagents used, that is excluding the copper solution, and check these periodically. The absorption of these solutions is measured on the Absorptiometer with 2 cm. cells as described previously.

(*b*) Copper percentage 0-0·25%

Take 25 ml. of the original copper solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution and to each volume add 4 ml. of spekker acid; colour up the solution as previously described under this heading. A corresponding blank determination must be carried out and the solutions checked periodically. The absorption of these solutions is measured with 4 cm. cells.

A typical calibration graph is shown in Fig. 12 obtained by using 2 cm. cells.

NOTES AND HINTS

(1) When calibrating and during an actual determination, it is important that the blank solution be prepared before the colour solution.

(2) It is not advisable to leave any of the solutions in the glass cells longer than necessary as the citrate tends to stain the glass. This may be removed by leaving the cells soaking overnight in nitric acid (S.G. 1·42).

(3) Higher ranges of copper should be determined by taking proportionately less quantity of the original alloy and not by dilution of the final solution.

LIMITS OF ACCURACY

An accuracy of ±1 per cent. of the copper content is obtained.

TIME FOR ONE DETERMINATION

10 to 15 minutes when treated in batches.

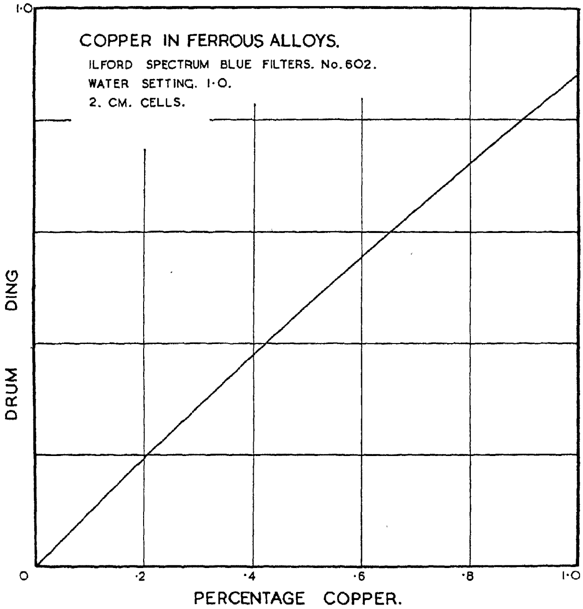


FIG. 12. Calibration graph for **COPPER** in ferrous alloys.

REFERENCE

F. W. Haywood and A. A. R. Wood. *The Analyst*, July 1943, vol. 68, pp. 206–208.

(B) DIRECT METHODS

It is not advisable to use direct methods with either the tungsten or mercury lamps. In the latter case there is no satisfactory waveband available, and, secondly, variables in the comparatively high blank reading would lead to errors.

Determination of Manganese in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in spekker acid and the manganese oxidised by the silver persulphate reaction to permanganic acid. Interference from other elements producing colours is obviated by decolorising the permanganic acid with sodium nitrite solution.

REAGENTS REQUIRED

Spekker acid	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid	S.G. 1·20.
Silver nitrate	2 per cent. solution.
Ammonium persulphate .	2·5 grm. solid or " Analoids."
Urea	0·5 grm. solid or " Analoids."
Sodium nitrite . . .	2 per cent. solution.
Potassium permanganate	Solution standardised to contain 0·25 grm. manganese per litre.
Iron	H.H.P. iron.

METHOD

Take 0·5 grm. of alloy in a 250 ml. conical beaker and dissolve in 20 ml. of spekker acid. Simmer to dissolve, and when the reaction ceases add 5 ml. of nitric acid and boil to expel nitrous fumes. If any carbides remain undissolved continue boiling until fumes of sulphur trioxide appear. Cool and make up to about 50 ml. with water. Add 10 ml. of 2 per cent. silver nitrate solution and 2·5 grm. of ammonium persulphate. Boil until the evolution of oxygen is complete, and cool. Add 0·5 grm. of urea, allow to dissolve, and make the solution up to 100 ml. with water. Measure the absorption of this solution using a 1 cm. cell and employing Ilford Spectrum Green filters No. 604 and a water setting of 1·0. Empty the cell, add one drop of sodium nitrite solution, fill up the cell with the original solution, and again measure the absorption of this solution as previously described. The difference between these two readings is proportional to the percentage of manganese in the alloy.

CALIBRATION GRAPH

Take 10 samples of 0·5 grm. of H.H.P. iron and dissolve in 20 ml. of spekker acid and proceed as given in the method prior to the oxidation phase. Add 1, 2, 3 up to 10 ml. of the standardised permanganate solution, then add silver nitrate and ammonium persulphate and proceed as stated previously under method. Measure the absorption of these solutions in 1 cm. cells. Plot a graph showing the relationship between difference drum divisions and percentage manganese.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of $KMnO_4$ solution required.
0–1% Mn.	0·5 cm.	2, 4, 6 up to 20.
0–0·5% Mn.	1·0 cm.	1, 2, 3 up to 10.
0–0·25% Mn.	2·0 cm.	0·5, 1·0, 1·5 up to 5.

Typical calibration graphs are shown in Fig. 7, Part I.

NOTES AND HINTS

(1) When determining manganese in high chromium steels (*e.g.* 18/8 and other austenitic steels) it may be found necessary to add more than 2·5 grm. of ammonium persulphate.

(2) When reducing the permanganic acid with sodium nitrite the urea reacts with the latter to produce small bubbles of nitrogen, which, if the cells are not scrupulously clean, adhere to the sides of the cell and give inaccurate readings. The cure for this is perfectly clean cells.

(3) Dust and organic matter must be excluded.

(4) Higher ranges of manganese may be determined by dilution either of the solution on a weight of 0·5 grm. or by taking an appropriately smaller weight of sample.

LIMITS OF ACCURACY

This method gives an accuracy of ±1 per cent. of the manganese content of the alloy.

TIME FOR ONE DETERMINATION

About 10 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, pp. 14, 15.

(B) DIRECT METHOD

(1) Tungsten Lamp

The procedure as given under (A) is followed exactly for the direct method omitting the blank reading.

(2) Mercury Lamp

The chemical procedure as outlined under (A) is followed exactly, except that no blank readings are required and Ilford Spectrum Yellow filters No. 606 are used.

The range covered is as follows :—

Range.	Size of Cell.
0–3·0% Mn.	0·5 cm.
0–1·5% Mn.	1·0 cm.
0–0·8% Mn.	2·0 cm.
0–0·4% Mn.	4·0 cm.

Typical calibration graphs for 0·5, 1·0, and 2·0 cm. cells are shown in Fig. 8, Part I.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis*. Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Molybdenum in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a sulphuric-phosphoric acid mixture, oxidised with nitric acid and the latter removed by fuming. The molybdenum is converted to the amber coloured thiocyanate, which is stabilised by the addition of perchloric acid.

REAGENTS REQUIRED

Spekker acid . . .	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid	S.G. 1·20.

Sodium nitrate .	0·5 grm. " Analoids."
Sulphuric acid .	25 per cent. solution.
Perchloric acid .	10 per cent. solution (made from 60 per cent. perchloric acid).
Stannous chloride	10 per cent. solution (10 grm. of $SnCl_2$ dissolved in 5 ml. HCl and diluted to 100 ml. with water).
Sodium thiocyanate	10 per cent. solution, or 0·5 grm. " Analoids."
Molybdenum . .	(*a*) MoO_3 solution standardised to contain 1 grm. of Mo per litre ; MoO_3 A.R. quality dissolved in ammonium hydroxide and made up to 1 litre with water. (*b*) B.C.S. Ferro-Molybdenum (No. 200) solution made up to contain 1 grm. of Mo per litre (see under Calibration). (*c*) H.H.P. molybdenum.
Iron	H.H.P. iron.

METHOD

Take 1·0 grm. of the alloy in a 250 ml. conical beaker and dissolve in 40 ml. of spekker acid. Simmer to dissolve and when the reaction ceases add 5 ml. of nitric acid or two 0·5 grm. sodium nitrate " Analoids " and boil to expel nitrous fumes. Continue boiling until fumes of sulphur trioxide appear, cool, and make up to 100 ml. with water.

(1) *Blank Solution*—Into a 100 ml. beaker add 10 ml. of the alloy solution, 10 ml. of sulphuric acid, 10 ml. of perchloric acid, 10 ml. of stannous chloride solution and 10 ml. of distilled water.

(2) *Colour Solution*—To another 100 ml. beaker add 10 ml. of the alloy solution, 10 ml. of sulphuric acid, 10 ml. of perchloric acid, 10 ml. of sodium thiocyanate solution or two " Analoids " and 10 ml. of distilled water, and finally 10 ml. of stannous chloride solution.

Allow these two solutions to stand for about fifteen minutes and measure the absorption of each solution using 1 cm. cells, Ilford Spectrum Blue-Green filters No. 603 and a water setting of 1·1. The difference between these two readings is proportional to the percentage of molybdenum in the alloy.

CALIBRATION GRAPH

Take eight samples each of 1·0 grm. of H.H.P. iron and dissolve in 40 ml. of spekker acid. Simmer to dissolve and when the reaction ceases add 5 ml. of nitric acid or two 0·5 grm. sodium nitrate "Analoids" and boil to expel all nitrous fumes.

Take either 0·2774 grm. of B.C.S. Ferro-Molybdenum (No. 200) or 0·2000 grm. of H.H.P. molybdenum, dissolve in *aqua regia*, add 10 ml. of spekker acid, and heat to fumes of sulphur trioxide. Dilute, cool, and make the solution up to 200 ml. with water. This solution now contains the equivalent of 1 grm. of Mo per litre or 0·001 grm. of Mo per ml., *i.e.* is equivalent to 0·1 per cent. Mo on a 1·0 grm. sample of alloy.

When the eight samples of 1·0 grm. of H.H.P. iron have dissolved add respectively 1, 2, 3 up to 8 ml. of the molybdenum solution. Dilute each solution up to 100 ml. with water; take two 10 ml. aliquots and prepare blank and colour solutions precisely as given under the method. Allow solutions to stand for about fifteen minutes and determine the absorptions as indicated previously. Plot a graph showing the relationship between difference drum readings and percentage molybdenum in the particular solution.

The complete range of cells is calibrated as follows:—

Range.	Size of Cell.	ml. of Molybdenum solution required
0–1·5% Mo.	0·5 cm.	2, 4, 6 up to 16.
0–0·8% Mo.	1·0 cm.	1, 2, 3 up to 8.
0–0·4% Mo.	2·0 cm.	0·5, 1·0, 1·5 up to 4.
0–0·2% Mo.	4·0 cm.	0·25, 0·5, 0·75 up to 2.

A typical calibration graph is shown in Fig. 13 using 1 cm. cells.

NOTES AND HINTS

(1) The cells must be absolutely chemically clean and entirely free from dust and organic matter.

(2) When determining molybdenum in excess of 1·5 per cent. proportionately less alloy must be taken and the balance made up with H.H.P. iron. For example, assume that an analysis for molybdenum is required on a substitute "66" high speed steel (*i.e.* 6 per cent. tungsten, 6 per cent. molybdenum), take 0·2 grm. of "66" steel and 0·8 grm. of H.H.P. iron, dissolve as already indicated, determine the percentage of molybdenum, multiplying the result from the calibration graph or the table of constants by 5.

(3) All nitric acid should be eliminated when fuming down as this contributes to fading of the final colour. If salts separate out these must be boiled into solution with water.

(4) All solutions must be made up and measured accurately and added in the order given under the method.

(5) The stannous chloride should be the purest obtainable and should be made up daily.

(6) If a solution of sodium thiocyanate is used, this should be freshly prepared. The use of 0·5 grm. " Analoids " overcomes this difficulty.

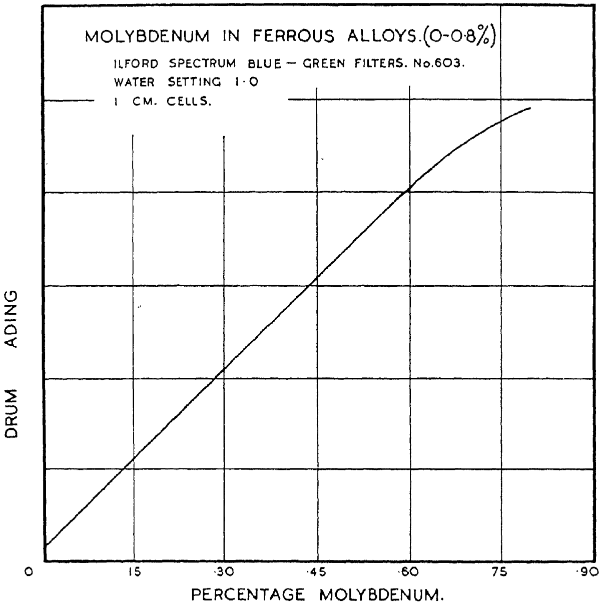


FIG. 13. Calibration graph for **MOLYBDENUM** in ferrous alloys.

(7) When a determination has been concluded it is important to empty and wash out the glass cells immediately, otherwise the stannous chloride causes staining of the glass.

(8) Copper in comparatively large amounts, *i.e.* greater than 0·5 per cent., will interfere by being precipitated as cuprous thiocyanate. In such cases this precipitate must be filtered off. Below 0·5 per cent. copper no interference is obtained.

(9) In order to reduce the time taken for a determination still further a sulphuric-perchloric acid mixture can be made using 62·5 ml. of sulphuric acid (S.G. 1·84) and 41·6 ml. of 60 per

cent. perchloric acid made up to 500 ml. with water. A 20 ml. fraction of this solution then contains the equivalent of 10 ml. of 25 per cent. sulphuric acid and 10 ml. of 10 per cent. perchloric acid.

LIMITS OF ACCURACY

Results are within ±1 per cent. of the molybdenum content of the alloy.

TIME FOR ONE DETERMINATION

About 20 minutes, but only when done in batches.

REFERENCES

(1) E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, pp. 17, 18.

(2) E. J. Vaughan. At lecture given to the Teesside Section of the Inst. of Chemistry, 21st October 1943.

(3) N. D. Ridsdale & Co., Ltd., Method Sheet No. 317, October 1943.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure is carried out as under (A) omitting to take blank readings.

(2) Mercury Lamp

Again this procedure is carried out as under (*B*) (1) using Ilford Spectrum Green filters No. 604, when the following ranges are obtained :—

Range.	Size of Cell.
0–2·0% Mo.	0·5 cm.
0–1·0% Mo.	1·0 cm.
0–0·5% Mo.	2·0 cm.
0–0·25% Mo.	4·0 cm.

Determination of Nickel in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a sulphuric-phosphoric acid mixture, oxidised with nitric acid and the nickel-dimethylglyoxime complex formed in ammoniacal solution, precipitation being prevented by the presence of iodine. Interference from metals insoluble in ammonia is obviated by the addition of citric acid. Readings are taken which are proportional to the percentage of nickel present in the alloy.

REAGENTS REQUIRED

Spekker acid . . .	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. of phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid	S.G. 1·20.
Ammonium citrate .	500 ml. of ammonium hydroxide (S.G. 0·88) is added to 500 grm. of citric acid until solution is complete and made up to 1 litre with water.
Iodine	N/10 solution.
Ammonium hydroxide	500 ml. of ammonium hydroxide (S.G. 0·88) made up to 1 litre with water.
Ammoniacal dimethylglyoxime .	1 grm. of dimethylglyoxime is dissolved in 500 ml. of ammonium hydroxide (S.G. 0·88) and made up to 1 litre with water.
Nickel sulphate . .	Solution is standardised to contain 0·100 grm. nickel per litre.
Nickel	H.H.P. nickel.

METHOD

Take 0·5 grm. of alloy in a 250 ml. conical beaker and dissolve in 20 ml. of spekker acid. Simmer to dissolve and when the reaction ceases add 5 ml. of nitric acid and boil to expel nitrous fumes. If any carbides remain undissolved continue boiling until fumes of sulphur trioxide appear. Cool, and make up the solution to 200 ml. with water. Take two 10 ml. aliquots and proceed as follows :—

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution and 20 ml. of ammonium hydroxide, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution, and 20 ml. of ammoniacal dimethylglyoxime solution, and make up to 100 ml. with water.

Measure the absorption of these two solutions using 1 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·2. The difference between these two readings is proportional to the percentage of nickel in the alloy.

CALIBRATION GRAPH

(1) *Blank Solution*—Take 10 ml. of water, add 1 ml. of spekker acid, and proceed as given under blank solution above.

(2) *Colour Solution*—Take 1, 2, 3 up to 10 ml. of the H.H.P. nickel solution or standardised nickel sulphate solution and to each add 1 ml. of spekker acid and proceed as given under the colour solution above.

Measure the absorption of each solution ; the difference in the absorptions between the colour solution and the blank solution plotted against the percentage nickel gives the calibration graph.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of $NiSO_4$ solution required.
0–8% Ni.	0·5 cm.	2, 4, 6 up to 20.
0–4% Ni.	1·0 cm.	1, 2, 3 up to 10.
0–2% Ni.	2·0 cm.	0·5, 1·0, 1·5 up to 5.
0–1% Ni.	4·0 cm.	0·25, 0·5, 0·75 up to 2·5.

A typical calibration graph is shown in Fig. 14 using 1 cm. cells.

NOTES AND HINTS

(1) It is very important that both when calibrating and doing an actual determination the blank solution should be prepared before the colour solution, thus excluding any possibility of the dimethylglyoxime being introduced into the blank solution.

(2) When obtaining a calibration graph using 4 cm. cells it is advisable to make up 50 ml. of the original nickel sulphate solution to 200 ml. with water and then to take off 1, 2, 3 up to 10 ml. of this solution for calibration.

(3) It is not advisable to leave any of these solutions in the glass cells for longer periods than is absolutely necessary, as the citrate tends to stain the glass. Should this occur the cells can be cleaned with concentrated nitric acid.

(4) Higher ranges of nickel should be determined by taking a proportionately less quantity of the original alloy and not by taking a 0·5 grm. sample and diluting the final solution.

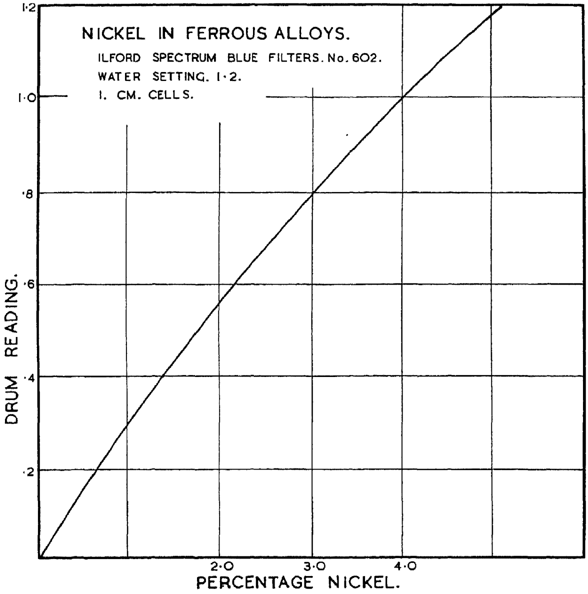


FIG. 14. Calibration graph for **NICKEL** in ferrous alloys.

LIMITS OF ACCURACY

This method gives an accuracy of ±1 per cent. of the nickel content of the alloy.

TIME FOR ONE DETERMINATION

About 8 to 10 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis*. Monograph published by Inst. of Chemistry, 1942, pp. 3, 4.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure as given under (A) is adopted, omitting to take blank solutions.

(2) Mercury Lamp

The same procedure is adopted as given under (B) (1) using Ilford Spectrum Green filters No. 604, when the follov obtained :—

Range.	Size of Cell.
0–8% Ni.	0·5 cm.
0–4% Ni.	1·0 cm.
0–2% Ni.	2·0 cm.
0–1% Ni.	4·0 cm.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Silicon in Steel

(A) DIFFERENCE METHOD

Tungsten Lamp

The steel is dissolved in dilute sulphuric acid, oxidised with permanganate and the silicon converted by the addition of ammonium molybdate to complex silico-molybdates, and these subsequently reduced by stannous chloride to molybdenum blue, the colour absorption of which is proportional to the silicon present in the steel.

REAGENTS REQUIRED

Sulphuric acid . . .	5 per cent. solution.
Potassium permanganate	3 per cent. solution.
Sulphurous acid . . .	Saturated solution.
Ammonium molybdate .	5 per cent. solution.
Sulphuric acid . . .	25 per cent. solution.
Stannous chloride . .	5 grm. of stannous chloride is dissolved in 6 ml. of hydrochloric acid (S.G. 1·12) and made up to 500 ml. with water.

Silicate solution	Solution standardised to contain 0·5 grm. of Si per litre. This is effected by taking 1·072 grm. of pure silica and fusing with sodium carbonate.
Iron	H.H.P. iron.

METHOD

Take 0·5 grm. of steel in a 400 ml. conical beaker, add 70 ml. of 5 per cent. sulphuric acid, simmer to dissolve, and when the reaction ceases add 15 ml. of potassium permanganate solution and continue boiling for two to three minutes. Reduce the excess of potassium permanganate with a few drops of sulphurous acid. Boil off the excess sulphur dioxide, cool, and make up to 250 ml. with water. Take two 20 ml. aliquot portions and treat as follows :—

(1) *Blank Solution*—Add 50 ml. of water, 20 ml. of 25 per cent. sulphuric acid, 10 ml. of ammonium molybdate solution and 10 ml. of stannous chloride solution ; stand for 15 minutes.

(2) *Colour Solution*—Add 50 ml. of water, 10 ml. of ammonium molybdate solution and stand for 5 minutes. Add 20 ml. of 25 per cent. sulphuric acid, 10 ml. of stannous chloride solution and stand for 15 minutes.

Measure off the absorptions of these solutions using 1 cm. cells, Ilford Spectrum Red filters No. 608 and a water setting of 1·2. The difference between the readings (1) and (2) is proportional to the percentage of silicon in the steel.

CALIBRATION GRAPH

Take ten 0·5 grm. samples of H.H.P. iron and dissolve each sample in 70 ml. of 5 per cent. sulphuric acid solution and proceed as given under method. Before diluting each to 250 ml. add respectively 0, 1, 2, 3 up to 10 ml. of the standardised silicate solution. Colour up as given under (2) and obtain difference readings as previously cited. Plot a graph showing drum difference readings against percentage silicon.

The range of cells employed is as follows :—

Range.	Size of Cell.	ml. of Silicate solution required.
0–1·5% Si.	0·5 cm.	0, 2, 4, 6 up to 20.
0–0·8% Si.	1·0 cm.	0, 1, 2, 3 up to 10.
0–0·4% Si.	2·0 cm.	0, 0·5, 1·0, 1·5 up to 5.
0–0·2% Si.	4·0 cm.	0, 0·25, 0·5 up to 2·5.

A typical calibration graph is shown in Fig. 15 using 1 cm. cells.

NOTES AND HINTS

(1) All solutions must be measured accurately.

(2) It is advisable to carry out a blank on all reagents from time to time.

LIMITS OF ACCURACY

Within ±1 per cent. of the silicon content of the steel.

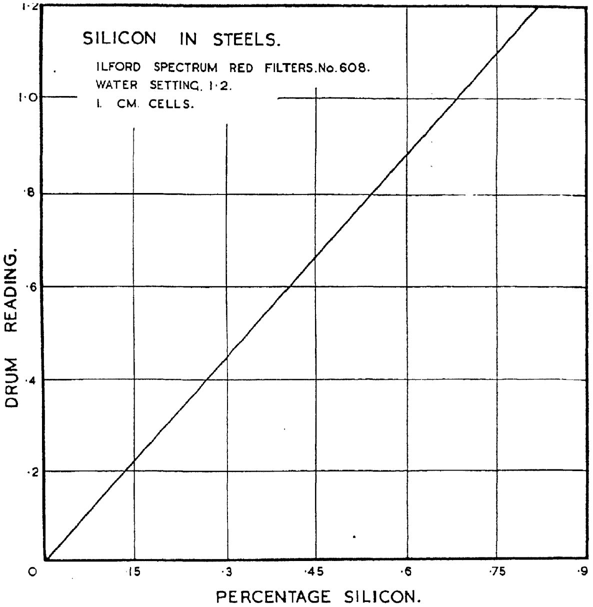


FIG. 15. Calibration graph for **SILICON** in steels.

TIME FOR ONE DETERMINATION

15 to 20 minutes when done in batches.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis*. Monograph published by Inst. of Chemistry, 1942, pp. 6, 7.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure as given under (A) is adopted, omitting to take blank solutions.

(2) Mercury Lamp

The same procedure as given under (B) (1) is adopted using Ilford Spectrum Yellow filters No. 606, when the following ranges are obtained :—

Range.	Size of Cell.
0–1·8% Si.	0·5 cm.
0–0·9% Si.	1·0 cm.
0–0·45% Si.	2·0 cm.
0–0·20% Si.	4·0 cm.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Titanium in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a sulphuric-nitric acid mixture and silicon removed by fuming and filtration. Titanium is determined in the filtrate by the addition of hydrogen peroxide to form the yellow pertitanic acid, the colour absorption of which is proportional to the percentage of titanium in the alloy. Vanadium and molybdenum interfere, but in the case of the latter a correction graph can be constructed.

The method cannot be used for the determination of titanium in the presence of vanadium.

REAGENTS REQUIRED

Sulphuric acid . . .	25 per cent. solution.
Sulphuric acid . . .	5 per cent. solution.
Nitric acid . . .	S.G. 1·42.

Hydrogen peroxide	20 vols.
Titanium solution	Standardised to contain 1·000 grm. of titanium per litre.
Molybdenum . .	(*a*) MoO_3 dissolved in ammonium hydroxide (S.G. 0·88) and standardised to contain 5 grm. per litre of molybdenum. (*b*) H.H.P. molybdenum.

METHOD

Take 1 grm. of the alloy in a 250 ml. squat beaker, add 80 ml. of 25 per cent. sulphuric acid solution, simmer to dissolve and when the reaction ceases add 10 ml. of nitric acid. Continue boiling until fumes of sulphur trioxide appear. Cool and add 20 ml. of 25 per cent. sulphuric acid solution, and after shaking round add 75 ml. of water. Carefully warm to dissolve salts, boil and filter through pulp, washing with 5 per cent. sulphuric acid solution. Cool the filtrate and make up to 200 ml. with water. Obtain a blank reading on this solution by filling a 1 cm. cell. Empty the cell, add 1 drop exactly of hydrogen peroxide and fill up the cell once more with the solution. Measure the absorption of these solutions using Ilford Spectrum Violet filters No. 601 and a water setting of 1·0.

The difference between these two readings is proportional to the percentage of titanium in the alloy.

CALIBRATION GRAPH

Titanium Graph—Take 0, 2, 4, 6 up to 20 ml. of the standardised titanium solution, to each add 10 ml. of 25 per cent. sulphuric acid solution and make each up to 200 ml. with water. Measure the absorption of these solutions after the addition of hydrogen peroxide as given under method. Plot the relationship between drum difference readings and percentage of titanium.

The complete range of cells is calibrated as follows :

Range.	Size of Cel	ml. of standardised titanium solution.
0–4% Ti.	0·5 cm.	0, 4, 8, 12 up to 40.
0–2% Ti.	1·0 cm.	0, 2, 4, 6 up to 20.
0–1·0% Ti.	2·0 cm.	0, 1, 2, 3 up to 10.
0–0·5% Ti.	4·0 cm.	0, 0·5, 1·0, 1·5 up to 5.

Molybdenum Correction Graph Take 0, 1, 2, 3 up to 10 ml. of the standardised molybdenum solution, representing respectively 0, 0·5, 1·0, 1·5 up to 5 per cent. molybdenum, to each add 10 ml. of 25 per cent. sulphuric acid solution and make up each solution to 200 ml. with water. After the addition of hydrogen peroxide measure the absorption of these solutions using the appropriate cells, Ilford

Spectrum Violet filters No. 601 and a water setting of 1·0. Plot the relationship between drum difference readings and percentage molybdenum.

A typical calibration graph for titanium using 1 cm. cells is shown in Fig. 16.

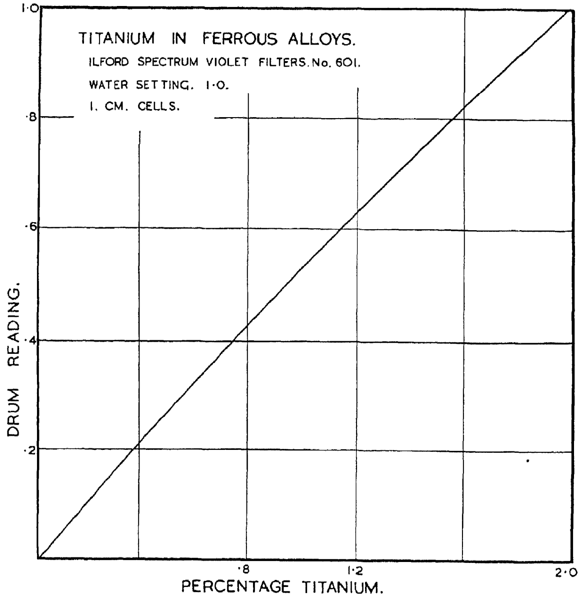


Fig. 16. Calibration graph for **TITANIUM** in ferrous alloys.

NOTES AND HINTS

(1) It is important always to take a blank reading before the colour solution.

(2) It has been found necessary, in order to obtain accurate repetitive results for titanium, to remove silicon. This method can be adopted to give the titanium and silicon contents by igniting the silica precipitate and applying the usual gravimetric technique.

(3) Care should be taken in fuming down to avoid loss due to sputtering.

LIMITS OF ACCURACY

An accuracy of ±1 per cent. of the titanium content of the ferrous alloy is obtained.

TIME FOR ONE DETERMINATION

20 to 30 minutes when done in batches.

REFERENCE

Private communication from G. R. Bolsover, Esq., Chief Metallurgist of Samuel Fox & Co., Ltd., Stocksbridge, near Sheffield.

(B) DIRECT METHOD

Direct methods are not advisable for this determination.

Determination of Vanadium in Ferrous Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a sulphuric-phosphoric acid mixture and the vanadium determined by adding hydrogen peroxide to an aliquot portion of the solution, thus forming pervanadic acid. Molybdenum and titanium interfere, but in the case of molybdenum a correction graph may be applied.

REAGENTS REQUIRED

Spekker acid .	150 ml. of sulphuric acid (S.G. 1·84) and 150 ml. phosphoric acid (S.G. 1·75) are made up to 1 litre with water.
Nitric acid . .	S.G. 1·20.
Hydrogen peroxide	10 vols.
Ammonium vanadate	Solution standardised to contain 0·25 grm. per litre of vanadium.
Molybdenum . .	(*a*) MoO_3 dissolved in ammonium hydroxide (S.G. 0·88) and standardised to contain 0·25 grm. of molybdenum per litre. (*b*) H.H.P. molybdenum.

METHOD

Take 0·5 grm. of the alloy in a 250 ml. conical beaker and add 40 ml. of spekker acid, simmer to dissolve and, when the reaction ceases, add 5 ml. of nitric acid. If any carbides remain undissolved continue boiling until fumes of sulphur trioxide appear. Cool and make up to 100 ml. with water and take two 50 ml. aliquots and proceed as follows :—

(1) *Blank Solution*—Add 2 ml. of water.
(2) *Colour Solution*—Add 2 ml. of hydrogen peroxide.

Measure the absorptions of these solutions using 4 cm. cells, Ilford Spectrum Violet filters No. 601 and a water setting of 1·0.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised vanadium solution and 10 ml. of spekker acid and make up to 50 ml. with water. To each solution add 2 ml. of hydrogen peroxide and plot a graph showing the relationship between drum difference readings and percentage of vanadium.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of vanadium solution required.
0–2% V.	2·0 cm.	0, 2, 4, 6 up to 20.
0–1% V.	4·0 cm.	0, 1, 2, 3 up to 10.

CORRECTION GRAPH FOR MOLYBDENUM

Take 5, 10, 15, and 20 ml. of the standardised molybdenum solution (representing respectively 0·5, 1·0, 1·5, and 2·0 per cent. molybdenum in the alloy) and add 10 ml. of spekker acid. Make up to 50 ml. with water and add 2 ml. of hydrogen peroxide. Measure the absorptions of these solutions using the appropriate cells, Ilford Spectrum Violet filters No. 601 and a water setting of 1·0. Plot a graph showing the relationship between drum difference readings and the percentage of molybdenum.

A typical calibration graph for vanadium using 4 cm. cells and the accompanying appropriate correction graph for molybdenum are shown on the one graph in Fig. 17.

NOTES AND HINTS

(1) All solutions must be measured accurately.
(2) It is important to keep hydrogen peroxide away from all blank solutions.

LIMITS OF ACCURACY

Within ±1 per cent. of the vanadium content of the alloy.

TIME FOR ONE DETERMINATION

5 to 10 minutes when done in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 20.

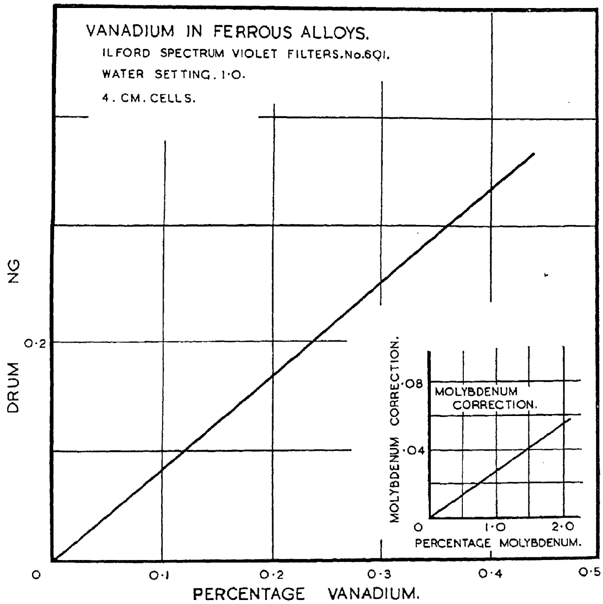


FIG. 17. Calibration graph for **VANADIUM** in ferrous alloys.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure as given under (A) is adopted, omitting to take blank solutions.

(2) Mercury Lamp

The procedure outlined in (B) (1) is used (the same filters

No. 601 being employed) and the complete range of cells is as follows :—

Range.	Size of Cell.
0–8·0% V.	0·5 cm.
0–4·0% V.	1·0 cm.
0–2·0% V.	2·0 cm.
0–1·0% V.	4·0 cm.

Chromium salts give a slight absorption in the wave-band employed and hence a correction graph must be constructed.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Composite Scheme of Analysis for Ferrous Alloys

It will be appreciated from the various methods already described that the opening out of the alloy is similar in the majority of cases. This lends itself to a composite scheme which is shown in Fig. 18.

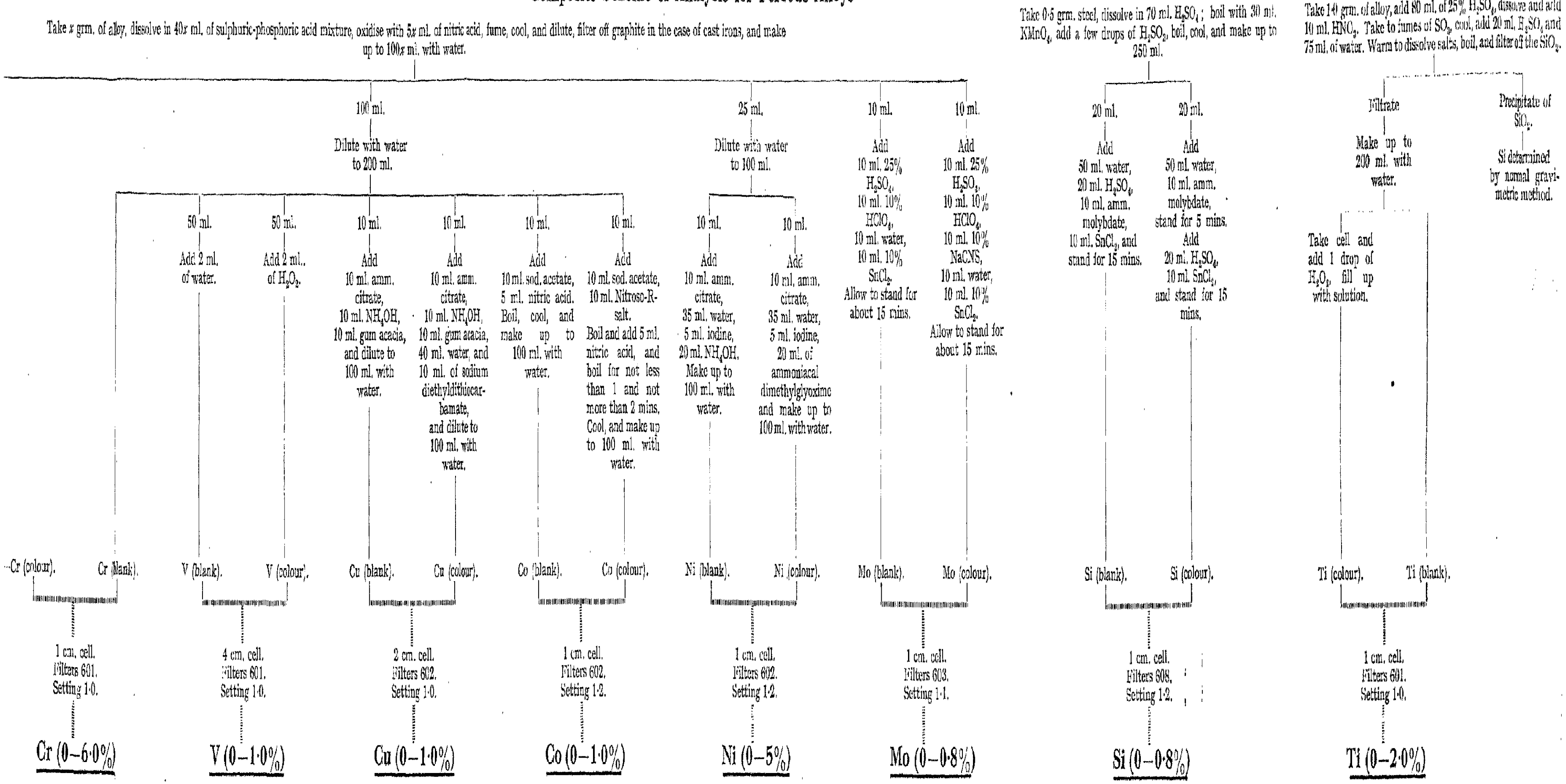
It is not always desired to carry out all the determinations cited under the ranges given, and the methods must be adjusted accordingly. The full ranges and particulars for each element are given under the specific methods.

An example will illustrate the operation of the composite scheme. An air-hardening tool steel is supposed to be of the following composition :—

Chromium, 10–11%
Nickel, 0·5–1·0%
Vanadium, 0·2–0·3%
Cobalt, 3·0%
Silicon, 0·2%
Carbon, 1·2–1·3%
Molybdenum, 0·5–0·7%
Manganese, 0·2%

A check analysis is required for chromium, cobalt, molybdenum, nickel, manganese, and vanadium. These analyses can be carried out on the Absorptiometer taking only one weighing. By reference to the methods given it is seen that the following cells and dilutions are required to give the ranges of the particular elements :—

Composite Scheme of Analysis for Ferrous Alloys



Take x grm. of alloy, dissolve in $40x$ ml. of sulphuric-phosphoric acid mixture, oxidise with $5x$ ml. of nitric acid, fume, cool, and dilute, filter off graphite in the case of cast irons, and make up to $100x$ ml. with water.

- Cr (colour). Cr (blank). 1 cm. cell. Filters 601. Setting 1·0. **Cr (0–6·0%)**
- 100 ml. Dilute with water to 200 ml.
  - 50 ml. Add 2 ml. of water. V (blank).
  - 50 ml. Add 2 ml. of H_2O_2. V (colour).
  - 4 cm. cell. Filters 601. Setting 1·0. **V (0–1·0%)**
  - 10 ml. Add 10 ml. amm. citrate, 10 ml. NH_4OH, 10 ml. gum acacia, and dilute to 100 ml. with water. Cu (blank).
  - 10 ml. Add 10 ml. amm. citrate, 10 ml. NH_4OH, 10 ml. gum acacia, 40 ml. water, and 10 ml. of sodium diethyldithiocarbamate, and dilute to 100 ml. with water. Cu (colour).
  - 2 cm. cell. Filters 602. Setting 1·0. **Cu (0–1·0%)**
  - 10 ml. Add 10 ml. sod. acetate, 5 ml. nitric acid. Boil, cool, and make up to 100 ml. with water. Co (blank).
  - 10 ml. Add 10 ml. sod. acetate, 10 ml. Nitroso-R-salt. Boil and add 5 ml. nitric acid, and boil for not less than 1 and not more than 2 mins. Cool, and make up to 100 ml. with water. Co (colour).
  - 1 cm. cell. Filters 602. Setting 1·2. **Co (0–1·0%)**
- 25 ml. Dilute with water to 100 ml.
  - 10 ml. Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. NH_4OH. Make up to 100 ml. with water. Ni (blank).
  - 10 ml. Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. of ammoniacal dimethylglyoxime and make up to 100 ml. with water. Ni (colour).
  - 1 cm. cell. Filters 602. Setting 1·2. **Ni (0–5%)**
- 10 ml. Add 10 ml. 25% H_2SO_4, 10 ml. 10% $HClO_4$, 10 ml. water, 10 ml. 10% $SnCl_2$. Allow to stand for about 15 mins. Mo (blank).
- 10 ml. Add 10 ml. 25% H_2SO_4, 10 ml. 10% $HClO_4$, 10 ml. 10% NaCNS, 10 ml. water, 10 ml. 10% $SnCl_2$. Allow to stand for about 15 mins. Mo (colour).
- 1 cm. cell. Filters 603. Setting 1·1. **Mo (0–0·8%)**

Take 0·5 grm. steel, dissolve in 70 ml. H_2SO_4; boil with 30 ml. $KMnO_4$, add a few drops of H_2SO_3, boil, cool, and make up to 250 ml.

- 20 ml. Add 50 ml. water, 20 ml. H_2SO_4, 10 ml. amm. molybdate, 10 ml. $SnCl_2$, and stand for 15 mins. Si (blank).
- 20 ml. Add 50 ml. water, 10 ml. amm. molybdate, stand for 5 mins. Add 20 ml. H_2SO_4, 10 ml. $SnCl_2$, and stand for 15 mins. Si (colour).
- 1 cm. cell. Filters 608. Setting 1·2. **Si (0–0·8%)**

Take 1·0 grm. of alloy, add 80 ml. of 25% H_2SO_4, dissolve and add 10 ml. HNO_3. Take to fumes of SO_3, cool, add 20 ml. H_2SO_4 and 75 ml. of water. Warm to dissolve salts, boil, and filter off the SiO_2.

- Filtrate. Make up to 200 ml. with water.
  - Take cell and add 1 drop of H_2O_2, fill up with solution. Ti (colour).
  - Ti (blank).
  - 1 cm. cell. Filters 601. Setting 1·0. **Ti (0–2·0%)**
- Precipitate of SiO_2. Si determined by normal gravimetric method.

COMPOSITE SCHEME

of

ANALYSIS

for

Cr, Co, Cu, Mn, Mo, Ni, Si, Ti, and V

in

FERROUS ALLOYS

Element.	Range.	Cells required.	ml. solution taken.
Cr.	0–12%	0·5 cm.	50 ml. of original solution.
Co.	3·0%	0·5 cm.	Dilute 100 ml. of original solution to 200 ml. and take two 5 ml. aliquots.
Mo.	0·5–0·7%	1·0 cm.	Two 10 ml. aliquots of original solution.
Ni.	0·5–1·0%	4·0 cm.	Dilute 25 ml. of original solution to 100 ml. and take two 10 ml. aliquots.
Mn.	0·2%	2·0 cm.	Same 50 ml. of original solution as used for Cr.
V.	0·2–0·3%	4·0 cm.	Dilute 100 ml. to 200 ml. and take two 50 ml. aliquots.

It will be noted from the above that 195 ml. of original solution are required for use as :—

(i) 50 ml. for Cr and Mn analysis.
(ii) 100 ml. for Co and V analysis.
(iii) 25 ml. for Ni analysis.
(iv) 20 ml. for Mo analysis.

Applying this to the composite scheme it will be seen that $100x$ ml. of solution is 195 ml., *i.e.*, x is 1·95. In actual practice x would be taken as 2. Thus the composite scheme can be used starting with an initial weight of steel of 2 grm.

CHAPTER VI

COPPER ALLOYS

The determinations given are for the following elements in copper alloys:—Copper, Iron, Manganese, Nickel, and Phosphorus.

As previously mentioned under ferrous alloys, only the best analytical reagents procurable should be used throughout all these determinations.

Determination of Copper in Copper Alloys

In this determination the application of the difference method is not necessary. The method was worked out using the direct method and with the tungsten lamp.

(B) DIRECT METHOD

Tungsten Lamp

The information given here is applicable to the determination of copper in brasses and bronzes of the usual ranges.

The alloy is dissolved in nitric acid and the copper coloured up with ammonia; iron, aluminium, and manganese are retained in solution by the addition of ammonium citrate.

REAGENTS REQUIRED

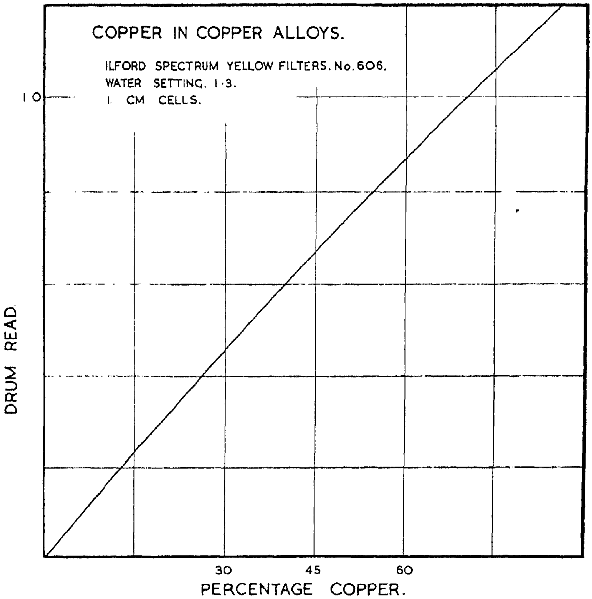
Nitric acid	S.G. 1·42.
Ammonium citrate . .	500 grm. of citric acid dissolved in 500 ml. of ammonia (S.G. 0·88) and made up to 1 litre with water.
Ammonium hydroxide	S.G. 0·88.
Copper	H.H.P. copper.

METHOD

Take 0·2 grm. of the alloy and dissolve it in 3 4 ml. of nitric acid. Boil to complete solution and expel nitrous fumes. Cool and dilute with 20 30 ml. of water. Add 5 ml. of ammonium citrate and 10 ml. of ammonium hydroxide, the latter from a burette, and make up to 100 ml. with water. In the case of a bronze, filter off the metastannic acid through a dry Whatman No. 1 filter paper sufficient solution to fill a 1 cm. glass cell (about 7 8 ml.). Measure off the absorption of this solution using 1 cm. cells, Ilford Spectrum Yellow filters No. 606 and a water setting of 1·3.

CALIBRATION GRAPH

Take 2 grm. of H.H.P. copper and dissolve in 30–40 ml. of nitric acid. Boil to complete solution and expel nitrous fumes, cool, and make up to 200 ml. with water. Take 2, 4, 6 up to 20 ml. of this solution and to each solution add 5 ml. of ammonium citrate and 10 ml. of ammonium hydroxide, the latter from a burette. Make each solution up to 100 ml. with water and measure off the absorptions as given under method. Construct a calibration graph showing the drum difference readings against the percentage copper.



19. Calibration graph for **COPPER** in copper alloys.

Only one size of cell, viz., 1 cm. size, is required for this determination.

A typical calibration graph is shown in Fig. 19 using 1 cm. cells only.

NOTES AND HINTS

(1) When the alloys are brasses and bronzes (not cupro-nickels) and contain small quantities of nickel, a small correction is required for the percentage of nickel present. This is obtained by constructing a correction graph using a nickel solution treated in the same manner as the copper solutions for the calibration graph. A subtraction of 0·01 drum division may be taken as equivalent to 2 per cent. nickel.

(2) It is essential to take all absorption readings within twenty minutes of making up to final volume, owing to fading of the colour.

LIMITS OF ACCURACY

This method gives an accuracy of at least ±1·0 per cent. of the copper content of the alloy.

TIME FOR ONE DETERMINATION

About 5 to 6 minutes for one determination when done in batches.

REFERENCE

Unpublished work in Research Laboratory of Wild-Barfield Electric Furnaces Ltd.

Alternative Method for the Determination of Copper in Brasses

(B) DIRECT METHOD

Tungsten Lamp

The alloy is dissolved in nitric acid, filtered if necessary, and the copper determined by the absorption of the actual solution in nitric acid.

REAGENTS REQUIRED

Nitric acid .	S.G. 1·42.
Brasses . .	Brasses of known copper contents, similar to the alloys under investigation.

METHOD

Take 2·0 grm. of the alloy as drillings, sawings, etc.—previously cleaned by magnetting—and place in a 250 ml. conical beaker. Add 5 ml. of nitric acid and 10 ml. of water. When dissolution is complete dilute to 50 ml. with water and boil for five minutes to remove nitrous fumes. Cool and make up to 100 ml. with water. Filter by means of double retentive paper sufficient of this solution to fill a 2 cm. cell and measure off the absorption of this solution using Ilford Spectrum Red filters No. 608 and a water setting of 1·2.

CALIBRATION GRAPH

Take 10 grm. of a brass of known copper content and dissolve in 25 ml. of nitric acid and 50 ml. of water. Boil to remove nitrous fumes, cool, dilute and filter the solution, and finally dilute to 100 ml. with water. Take 2, 4, 6 up to 20 ml. of this solution, diluting each to 100 ml. with water and determine the absorption of each solution as given under method. Construct a calibration graph showing the drum readings against the percentage copper.

NOTES AND HINTS

(1) It is only necessary to use one size of cell, namely 2 cm.

(2) It is advisable to prepare separate calibration graphs for the various ranges of brasses, namely 50/50, 60/40, 70/30, 80/20, and 90/10 CuZn.

LIMITS OF ACCURACY

This method gives an accuracy of ±1 per cent. of the copper content of the brass.

TIME FOR ONE DETERMINATION

About 5 minutes when done in batches.

REFERENCE

Unpublished work.

Determination of Iron in Copper Alloys

A difference method is not applicable to this determination and a direct method using the tungsten lamp only is cited.

(B) DIRECT METHOD

Tungsten Lamp

The method given is applicable to the determination of iron in brasses, bronzes, gun metals, cupro-nickels, etc.

The alloy is dissolved in a nitric-sulphuric acid mixture and the nitric acid subsequently fumed off. Iron is determined in an aliquot portion by the thiocyanate reaction. In order to keep copper in solution an excess of hydrochloric acid is added ; the colour due to cupric thiocyanate is allowed for by the construction of a correction graph.

REAGENTS REQUIRED

Sulphuric acid . . .	25 per cent. solution.
Nitric acid	S.G. 1·42.
Hydrochloric acid . .	S.G. 1·18.
Ammonium persulphate .	0·5 per cent. solution.
Sodium thiocyanate . .	20 per cent. solution.
Iron	Solution prepared by dissolving 0·75 grm. of H.H.P. iron in a minimum quantity of nitric acid and making up to 1 litre with water.
Copper	H.H.P. copper.

METHOD

Take 0·5 grm. of the copper alloy and dissolve by adding accurately 10 ml. of sulphuric acid solution and 2–3 ml. of nitric acid (S.G. 1·42). Heat, and when solution is complete boil to remove nitrous fumes and continue heating until fumes of sulphur trioxide appear, but avoid spattering. Cool, add 10 ml. of hydrochloric acid. Heat if necessary to dissolve salts, cool, and make up to 100 ml. with water. Take a 10 ml. aliquot, add 50 ml. of water and 10 ml. of ammonium persulphate solution and 10 ml. of sodium thiocyanate solution. Make up the solution to 100 ml., allow to stand for 15 minutes, and then measure off the absorption using 1 cm. cells, Ilford Spectrum Green filters No. 604 and a water setting of 1·0.

Subtract the appropriate blank for the percentage of copper present in the alloy (see Calibration).

CALIBRATION GRAPHS

(*a*) *Graph for Iron*.—Take 0, 1, 2, 3 up to 10 ml. of the iron solution, add 10 ml. of 25 per cent. sulphuric acid to each solution, fume down, and then proceed exactly as given under the method. Similarly allow the solutions to stand for 15 minutes before measuring off the absorptions as given previously.

Construct the graph showing the relationship between drum readings and percentage of iron, in the appropriate solutions.

(*b*) *Graph for Copper*—Take 0·1, 0·2, 0·3 up to 0·5 grm. of copper, dissolve and colour up as given under method.

Construct a calibration graph of drum readings against percentage copper in each solution using 1 cm. cells. As a general rule this calibration graph over the whole range of 0–100 per cent. copper is a straight line covered by only 0·10 of a drum division.

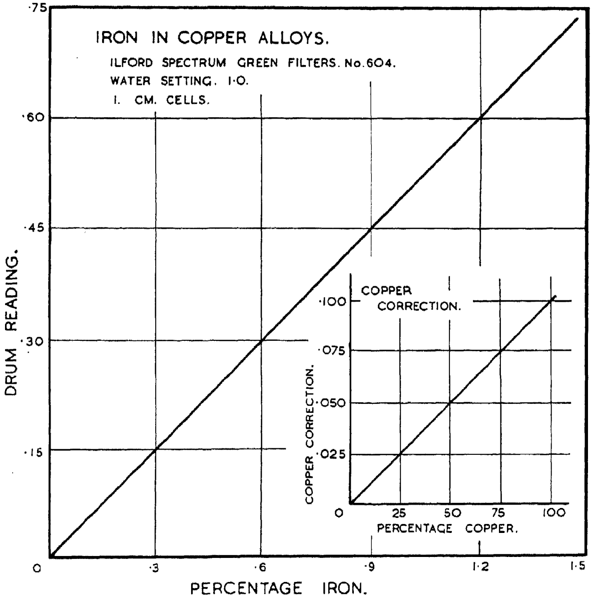


Fig. 20. Calibration graph for **IRON** in copper alloys.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of iron solution required.	Copper required.
0–3·0% Fe.	0·5 cm.	0, 2, 4, 6 up to 20.	For all ranges take the same solutions, namely, 0·1, 0·2 up to 0·5 grm. of copper.
0–1·5% Fe.	1·0 cm.	0, 1, 2, 3 up to 10.	
0–0·75% Fe.	2·0 cm.	0, 0·5, 1·0 up to 5.	
0–0·4% Fe.	4·0 cm.	0, 0·25, 0·5 up to 2·5.	

The typical calibration graphs obtained are shown in Fig. 20.

NOTES AND HINTS

(1) As slight fading of the iron thiocyanate may occur it is advisable to work on a fairly strict time basis.

(2) For calibration of 2 cm. and 4 cm. cells it is advisable to take twofold and fourfold dilutions respectively of the original iron solution and then add 0, 1, 2, 3 up to 10 ml. of each solution for the respective calibration graphs.

(3) A blank on the reagents should be taken from time to time.

(4) The concentration of the thiocyanate solution should be controlled by diluting 10 ml. of the original solution to 200 ml. and titrating against N/10 silver nitrate solution. The titre should be within 2–3 per cent. of the reading taken when obtaining the original calibration graph.

LIMITS OF ACCURACY

This method gives an accuracy of per cent. of the iron content of the copper alloy.

TIME FOR ONE DETERMINATION

About 8 to 10 minutes when done in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, pp. 30, 31.

Determination of Manganese in Copper Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

This method is suitable for brasses, gun metals, nickel silvers, bronzes, including manganese bronze and aluminium bronze, cupro-nickels, etc.

Solution of the alloy is effected in a nitric-sulphuric acid mixture followed by the periodate oxidation to convert the manganese to permanganic acid. Interference from other elements producing colours is obviated by decolorising the permanganic acid with sodium nitrite and taking difference readings.

REAGENTS REQUIRED

Sulphuric acid	25 per cent.
Nitric acid	S.G. 1·42.
Potassium periodate . .	0·3 grm. solid or "Analoids."
Sodium nitrite	2 per cent. solution.
Potassium permanganate .	Solution standardised to contain 0·25 grm. manganese per litre.
Copper	H.H.P. copper.

METHOD

Take 0·5 grm. of the copper alloy in a 250 ml. conical beaker, dissolve in 10 ml. of 25 per cent. sulphuric acid with 5 ml. of nitric acid and warm until solution is complete. Boil to expel nitrous fumes, add 0·3 grm. of potassium periodate and maintain at boiling point for 5 to 10 minutes for complete oxidation. Cool, make up to 100 ml. with water and measure the absorption of this solution using 1 cm. glass cells, Ilford Spectrum Green filters No. 604, and a water setting of 1·0. Empty the glass cell, add 1 drop of sodium nitrite, fill up with the coloured solution and again measure the absorption of this solution as previously described. The difference between these two readings is proportional to the percentage of manganese in the copper alloy.

CALIBRATION GRAPH

Take 10 samples each of 0·5 grm. of H.H.P. copper, dissolve as given in the method, and prior to the periodate oxidation add respectively 1, 2, 3 up to 10 ml. of standardised potassium permanganate solution. To each solution add 0·3 grm. of potassium periodate and treat as before. Measure the absorptions of these solutions as cited previously.

The complete range of cells is calibrated as follows :--

Range.	Size of Cell.	ml. of $KMnO_4$ required.
0 1% Mn.	0·5 cm.	2, 4, 6 up to 20.
0 0·5% Mn.	1·0 cm.	1, 2, 3 up to 10.
0 0·25% Mn.	2·0 cm.	0·5, 1·0, 1·5 up to 5.

A typical calibration graph, using 1 cm. cells, is shown in Fig. 21.

NOTES AND HINTS

(1) All dust and organic matter must be excluded.

(2) Copper gives a slight increase in the light absorption of the permanganic acid, but this is constant, above a minimum amount of copper.

LIMITS OF ACCURACY

This is within ±1 per cent. of the manganese content of the alloy.

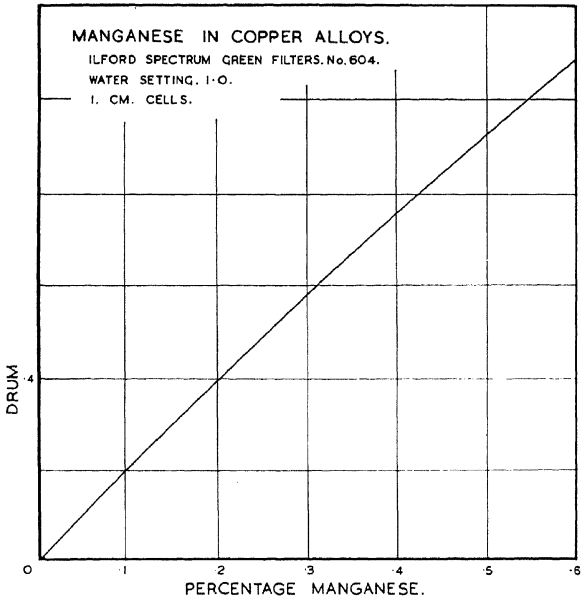


FIG. 21. Calibration graph for **MANGANESE** in copper alloys.

TIME FOR ONE DETERMINATION

5 to 10 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, pp. 28, 29, 30.

Determination of Nickel in Copper Alloys

This method is only applicable for nickel contents up to 5 per cent.

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a nitric-sulphuric acid mixture and the nickel determined in an aliquot portion by the addition of ammoniacal dimethylglyoxime solution and iodine. The coloration produced is proportional to the percentage of nickel in the alloy.

REAGENTS REQUIRED

Sulphuric acid	25 per cent.
Nitric acid	S.G. 1·42.
Ammonium citrate	500 ml. of ammonium hydroxide (S.G. 0·88) is added to 500 grm. of citric acid until solution is complete and made up to 1 litre with water.
Iodine	N/10 solution.
Ammonium hydroxide	500 ml. of ammonium hydroxide (S.G. 0·88) made up to 1 litre with water.
Ammoniacal dimethylglyoxime	1 grm. of dimethylglyoxime is dissolved in 500 ml. of ammonium hydroxide (S.G. 0·88) and made up to 1 litre with water.
Nickel	(*a*) Solution standardised to contain 0·100 grm. of nickel per litre, made up from the sulphate. (*b*) H.H.P. nickel.

METHOD

Take 0·25 grm. of the alloy in a 250 ml. conical beaker, dissolve in 10 ml. of sulphuric acid and 5 ml. of nitric acid. Warm to dissolve and if tin separates out take to fumes of sulphur trioxide. Cool, make up to 100 ml. with water, and take two 10 ml. aliquots and treat as follows:

(1) *Blank Solution* Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution, and 20 ml. of ammonium hydroxide and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution, and 20 ml. of ammoniacal dimethylglyoxime solution and make up to 100 ml. with water. Allow this solution to stand between 10 to 20 minutes and then measure the absorption of these two solutions using 1 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The difference between these two readings is proportional to the percentage of nickel in the copper alloy.

CALIBRATION GRAPH

(1) *Blank Solution*—Take 10 ml. of water, add 1 ml. of sulphuric acid, and proceed exactly as given under the blank.

(2) *Colour Solution*—Take 1, 2, 3 up to 10 ml. of the H.H.P. nickel solution or the standardised nickel sulphate solution, to each add 1 ml. of sulphuric acid and proceed as given under method for the colour solution.

Measure the absorptions of these respective solutions, the difference plotted against the percentage nickel giving the calibration graph.

The complete range of cells is calibrated as follows :—

Range.	Size of Cell.	ml. of $NiSO_4$ solution required.
0–4% Ni.	1·0 cm.	1, 2, 3 up to 10.
0–2% Ni.	2·0 cm.	0·5, 1·0, 1·5 up to 5.
0–1% Ni.	4·0 cm.	0·25, 0·5, 0·75 up to 2·5.

A typical calibration graph is shown in Fig. 14 using 1 cm. cells. The calibration graph for nickel in copper alloys is identical with the same graph for nickel in ferrous alloys, when using the same Absorptiometer.

NOTES AND HINTS

(1) It is very important that both when calibrating and doing an actual determination the blank solution should be prepared before the colour solution, thus excluding any possibility of the dimethylglyoxime being introduced into the blank solution.

(2) When obtaining a calibration graph using 4 cm. cells it is advisable to make up 50 ml. of the original nickel sulphate solution to 200 ml. with water and then to take off 1, 2, 3 up to 10 ml. of this solution for calibration.

(3) It is not advisable to leave any of these solutions in the glass cells for longer periods than is absolutely necessary, as the citrate tends to stain the glass. Should this occur the cells can be cleaned with concentrated nitric acid.

(4) It is important that the absorption of the colour solution should be measured within 10 to 20 minutes of production of the colour. This is because copper also produces a colour with dimethylglyoxime, but this is destroyed on standing; in addition the copper appears to inhibit the fading of the nickel complex, but this reaction does not begin until 20 to 30 minutes after the expiry of the production of colour.

(5) In many laboratories a composite scheme of analysis for copper alloys is in vogue which involves the separation of the copper, *e.g.*, by electrolysis. In such cases nickel may be determined in the filtrate by the method already given, provided a correct aliquot portion is taken. Wherever possible, this method, which is not so critical, is preferable to the procedure outlined above.

LIMITS OF ACCURACY

(*a*) *Method as given*—Within ±2 per cent. of the nickel content of the copper alloy.

(*b*) *Copper separated*—If methods similar to those indicated under (5) in Notes and Hints are employed, then a standard accuracy of ±1 per cent. of the nickel content of the alloy is obtained.

TIME FOR ONE DETERMINATION

About 10 to 15 minutes when treated in batches.

REFERENCE

Application of E. J. Vaughan's method for steel as applied in the Research Laboratory of Wild-Barfield Electric Furnaces Ltd.

(B) DIRECT METHODS

It is only advisable to employ direct methods for this determination when the copper has been separated from the alloy. In such cases the information given under (B) page 65 for nickel in ferrous alloys applies.

Determination of Phosphorus in Copper Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a nitric-sulphuric acid mixture, the phosphorus being oxidised to phosphoric acid by means of potassium permanganate solution. The phosphoric acid is converted to the phospho-molybdate complex by the addition of ammonium molybdate, and the complex subsequently reduced with stannous chloride to molybdenum blue. The intensity of this colour is proportional to the percentage of phosphorus present in the alloy.

REAGENTS REQUIRED

Sulphuric acid	25 per cent. solution.
Sulphuric acid	20 per cent. solution.
Nitric acid	S.G. 1·42.
Potassium permanganate	1 per cent. solution.
Hydrobromic acid	46/48 per cent. HBr.
Ammonium molybdate	Dissolve 10 grm. in 100 ml. of water and pour into 80 ml. of 25 per cent. sulphuric acid and make up to 200 ml. with water.
Stannous chloride	Dissolve 1 grm. in 1·6 ml. of concentrated hydrochloric acid and make up to 100 ml. with water. The solution used in this method is obtained by taking 10 ml. of the above solution and diluting to 200 ml. with water.
Phosphate solution	Disodium hydrogen phosphate—standardised to contain 0·01 grm. of phosphorus per litre.

METHOD

(*a*) Phosphorus content 0·01-0·1%

Take 0·5 grm. of the alloy in a 250 ml. conical beaker, add 40 ml. of 25 per cent. sulphuric acid and 2-3 ml. of nitric acid, warm to dissolve and boil off nitrous fumes. Add 1 ml. of potassium permanganate solution and continue heating until fumes of sulphur trioxide just appear. Remove from the hot plate, add 0·5 ml. of hydrobromic acid and again fume down until all the bromine is removed and sulphur trioxide is again evident. Cool and make up to 50 ml. with water and take two 10 ml. aliquot portions and proceed as follows:

(1) *Blank Solution*—Add 10 ml. of stannous chloride and make up to 100 ml. with water.

(2) *Colour Solution*—Add 60 ml. of water, 10 ml. of ammonium molybdate, 10 ml. of stannous chloride, and make up to 100 ml. with water and stand for 10 minutes.

Measure off the absorptions of these solutions using 2 cm. cells, Ilford Spectrum Red filters No. 608, and a water setting of 1·3.

The difference in the readings obtained for these two solutions is proportional to the amount of phosphorus present in the alloy.

(*b*) Phosphorus content 0·1-1·0%

Take 0·5 grm. of the alloy in a 650 ml. conical beaker, add 40 ml. of 25 per cent. sulphuric acid and 2–3 ml. of nitric acid, warm to dissolve and boil off nitrous fumes. Add 1 ml. of potassium permanganate solution and continue heating until fumes of sulphur trioxide just appear. Remove from the hot plate, add 0·5 ml. of hydrobromic acid and again fume down until all the bromine is removed and sulphur trioxide is again evident. Cool and make up to 500 ml. with water and take two 10 ml. aliquot portions and proceed as follows :—

(1) *Blank Solution*—Add 10 ml. of 20 per cent. sulphuric acid, 10 ml. of stannous chloride, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of 20 per cent. sulphuric acid, 50 ml. of water, 10 ml. of ammonium molybdate, and 10 ml. of stannous chloride, make up to 100 ml. with water and stand for 10 minutes.

Measure off the absorptions of these two solutions as given previously under method (*a*).

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised phosphate solution and treat as for the alloy given in method (*b*) above.

Stand all solutions for 10 minutes and measure the absorptions as previously indicated. Plot the results of drum difference readings against percentage phosphorus. Only one graph is necessary and this same graph covers the ranges previously described, viz., phosphorus 0·01–0·1 per cent. and 0·1–1·0 per cent.

The range of cells required is calibrated as follows :—

Range.	Size of Cell.	ml. of phosphate solution required.	Method.
0–2·0% P.	1 cm.	0, 2, 4, 6 up to 20	(*b*)
0–1·0% P.	2 cm.	0, 1, 2, 3 up to 10	(*b*)
0–0·1% P.	2 cm.	0, 1, 2, 3 up to 10	(*a*)
0–0·2% P.	1 cm.	0, 2, 4, 6 up to 20	(*a*)

A typical calibration graph using method (*b*) and 2 cm. cells is shown in Fig. 22.

NOTES AND HINTS

(1) The method is somewhat critical and acid concentrations should be maintained accurately throughout.

(2) Avoid loss of sulphuric acid when fuming down.

(3) Stannous chloride should be freshly prepared from day to day and checked occasionally against a standard iodine solution.

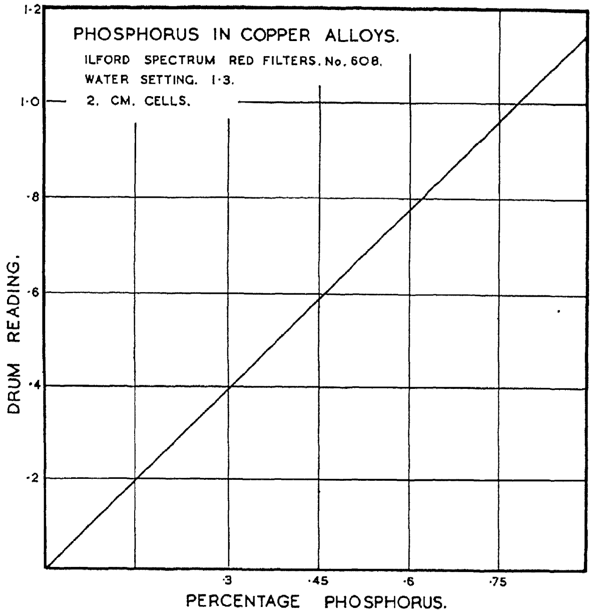


FIG. 22. Calibration-graph for **PHOSPHORUS** in copper alloys.

(4) When carrying out determinations it is advisable to obtain a blank using all the reagents but no alloy. This is in order to check up on any phosphorus which may be present in the reagents, and the appropriate blank must be subtracted from the reading obtained.

LIMITS OF ACCURACY

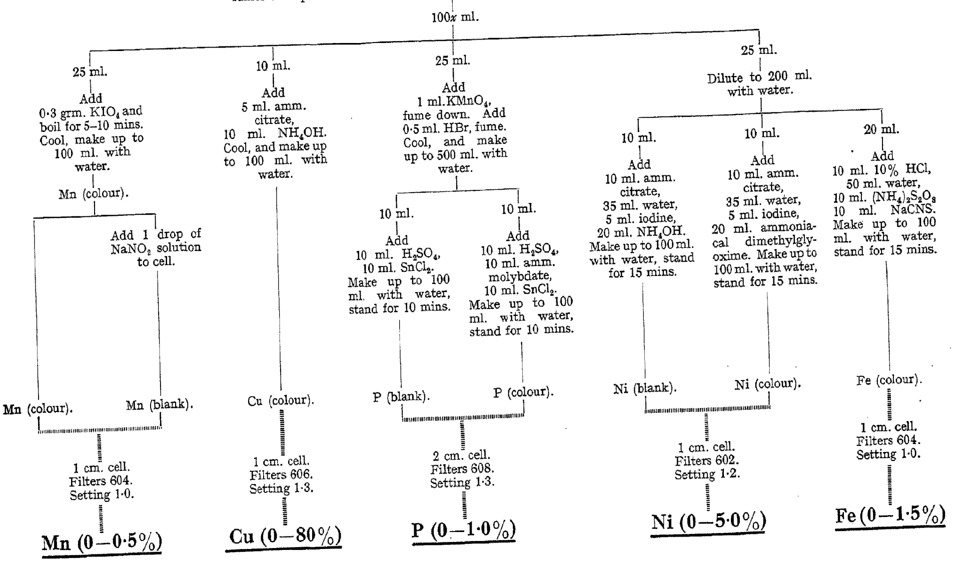
Results obtained are within ±1 per cent. of the phosphorus content of the alloy.

COMPOSITE SCHEME
of
# ANALYSIS
for
Cu, Fe, Mn, Ni, and P
in
COPPER ALLOYS

Fig. 23

Composite Scheme of Analysis for Copper Alloys

Take $2x$ grm. of alloy, dissolve in $40x$ ml. of 25% H_2SO_4 and $(25–30)x$ ml. HNO_3. Warm to complete solution and heat till fumes of sulphur trioxide appear. Cool, and make up to $100x$ ml. with water.


100x ml.
25 ml.
Add 0·3 grm. KIO_4 and boil for 5–10 mins. Cool, make up to 100 ml. with water.
Mn (colour).
Add 1 drop of $NaNO_2$ solution to cell.
Mn (colour).
Mn (blank).
1 cm. cell. Filters 604. Setting 1·0.
Mn (0—0·5%)
10 ml.
Add 5 ml. amm. citrate, 10 ml. NH_4OH. Cool, and make up to 100 ml. with water.
Cu (colour).
1 cm. cell. Filters 606. Setting 1·3.
Cu (0—80%)
25 ml.
Add 1 ml. $KMnO_4$, fume down. Add 0·5 ml. HBr, fume. Cool, and make up to 500 ml. with water.
10 ml.
Add 10 ml. H_2SO_4, 10 ml. $SnCl_2$. Make up to 100 ml. with water, stand for 10 mins.
P (blank).
10 ml.
Add 10 ml. H_2SO_4, 10 ml. amm. molybdate, 10 ml. $SnCl_2$. Make up to 100 ml. with water, stand for 10 mins.
P (colour).
2 cm. cell. Filters 608. Setting 1·3.
P (0—1·0%)
25 ml.
Dilute to 200 ml. with water.
10 ml.
Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. NH_4OH. Make up to 100 ml. with water, stand for 15 mins.
Ni (blank).
10 ml.
Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. ammoniacal dimethylglyoxime. Make up to 100 ml. with water, stand for 15 mins.
Ni (colour).
1 cm. cell. Filters 602. Setting 1·2.
Ni (0—5·0%)
20 ml.
Add 10 ml. 10% HCl, 50 ml. water, 10 ml. $(NH_4)_2S_2O_8$ 10 ml. NaCNS. Make up to 100 ml. with water, stand for 15 mins.
Fe (colour).
1 cm. cell. Filters 604. Setting 1·0.
Fe (0—1·5%)

TIME FOR ONE DETERMINATION

About 10 to 15 minutes when done in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 32.

(B) DIRECT METHOD

Tungsten Lamp

For most alloys, the blank will be the same for the particular range being employed. Thus a direct method may be used following the procedures under (A) and omitting the blank reading.

Composite Scheme of Analysis for Copper Alloys

A composite scheme of analysis, shown in Fig. 23, has been worked out for copper alloys in a similar manner to that evolved for ferrous alloys.

It is not always necessary to carry out all the determinations given under the ranges cited, and the methods must be adjusted accordingly. The full ranges and particulars for each element are given under the specific methods.

It is not deemed necessary to quote a definite example, as the ranges given for the elements for copper alloys are those normally encountered in industry.

CHAPTER VII

ALUMINIUM ALLOYS

The determinations given are for the following elements in commercial aluminium alloys: Copper, Iron, Manganese, Nickel, Silicon, and Titanium.

In every method cited it is advisable to use only the best analytical quality reagents obtainable.

The normal method for solution of the alloy is by the use of sodium hydroxide solution, followed by acidification with nitric acid. With alloys containing 10 to 14 per cent. silicon it is advisable to filter off any silica which may separate out and proceed in the normal manner with the filtrate.

Determination of Copper in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda, the solution acidified with nitric acid and copper determined by the formation of the diethyldithiocarbamate complex in ammoniacal solution. Metals insoluble in ammonia are held in solution by the use of citric acid.

REAGENTS REQUIRED

Caustic soda	10 per cent. solution.
Nitric acid	S.G. 1·42.
Ammonium citrate . .	500 ml. of ammonium hydroxide (S.G. 0·88) is added to 500 grm. of citric acid until solution is complete, and made up to 1 litre with water.
Ammonium hydroxide	200 ml. of ammonium hydroxide (S.G. 0·88) is made up to 1 litre with water.
Colloid	1·0 grm. of gum acacia is dissolved in 100 ml. of hot water and the solution made up to 200 ml. with water.
Sodium diethyldithiocarbamate . . .	0·50 grm. is made up to 250 ml. with water.
Copper	H.H.P. copper.

METHOD

(*a*) Copper percentage 0-1% and 0-5%

For alloys containing up to 1 per cent. copper, take 0·5 grm. of the alloy—for higher concentrations of copper take proportionately less quantities in a 250 ml. conical beaker—add 20 ml. of 10 per cent. caustic soda solution, heat to dissolve, acidify with 10 ml. of nitric acid, and boil to complete solution and expel nitrous fumes. Cool to room temperature and make up to 100 ml. with water. Take two 10 ml. aliquot portions and proceed as follows :—

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide, 10 ml. of gum acacia, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and 40 ml. of water. Shake well and then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up the volume to 100 ml. with water.

Measure the absorption of these solutions using 2 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The difference between (1) and (2) represents the colour due to copper and is read off on the appropriate calibration graph.

(*b*) Copper percentage 0–0·25%

The alloy sample of weight 0·5 grm. is dissolved and made up as described under method (*a*). Take two 20 ml. aliquot portions and proceed as follows :—

(1) *Blank Solution*—Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and shake well ; then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up to 100 ml. with water.

Measure the absorption of these solutions by means of 4 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The difference between (1) and (2) represents the colour due to copper.

CALIBRATION GRAPH

(*a*) Copper percentage 0-1% and 0-5%

Take 0·50 grm. of H.H.P. copper and dissolve in 10 ml. of nitric acid (S.G. 1·42), boil to expel nitrous fumes, and make up to 1 litre with water. Take 50 ml. of this solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution, and to each volume add 2 ml. of 10 per cent. caustic soda and 1 ml. of nitric acid and colour up the solution as previously described under (*a*) (2). At the same time carry out a blank determination of the normal reagents used, that is excluding the copper solution, and check these periodically. The absorption of these solutions is measured on the Absorptiometer with 2 cm. cells as described previously.

(*b*) Copper percentage 0-0·25%

Take 25 ml. of the original copper solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution and to each volume add 4 ml. of caustic soda solution and 2 ml. of nitric acid and colour up the solution as previously described under this heading. A corresponding blank determination must be carried out and the solutions checked periodically. The absorption of these solutions is measured with 4 cm. cells as described under (*b*) (2).

Calibration graphs for copper as given under ferrous alloys, Fig. 12, Part II, apply equally well for aluminium alloys.

NOTES AND HINTS

(1) When calibrating and during an actual determination, it is important that the blank solution shall be prepared before the colour solution.

(2) It is not advisable to leave any of the solutions in the glass cells longer than necessary as the citrate tends to stain the glass. This may be removed by leaving the cells soaking overnight in nitric acid (S.G. 1·42).

(3) Higher ranges of copper should be determined by taking proportionately less quantity of the original aluminium alloy and not by dilution of the final solution.

LIMITS OF ACCURACY

An accuracy of ±1 per cent. of the copper content of the aluminium alloy is obtained.

TIME FOR ONE DETERMINATION

10 to 15 minutes when treated in batches.

REFERENCE

F. W. Haywood and A. A. R. Wood. Adaptation of method described in *The Analyst*, vol. 68, July 1943, pp. 206–208.

(B) DIRECT METHOD

(1) Tungsten Lamp

It is not considered advisable to apply the direct method to this determination for the reasons given on page 54.

Determination of Iron in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda and the solution acidified with nitric acid. An aliquot is taken and the iron coloured up by means of sodium thiocyanate.

REAGENTS REQUIRED

Caustic soda . .	10 per cent. solution.
Nitric acid . . .	S.G. 1·42.
Sulphuric acid . .	25 per cent. solution.
Sodium thiocyanate	20 per cent. solution.
Aluminium . . .	H.H.P. aluminium.
Iron	Solution made up by dissolving 0·100 grm. of H.H.P. iron in the minimum quantity of nitric acid and making up to 1 litre with water.

METHOD

Take 0·5 grm. of the aluminium alloy in a 250 ml. conical beaker, digest in 20 ml. of sodium hydroxide solution until the reaction ceases. Add 10 ml. of water and 10 ml. of nitric acid with due caution and boil to complete solution and expel nitrous fumes. Cool, and make up to 100 ml. with water. Take two 20 ml. aliquots and proceed as follows :—

(1) *Blank Solution*—Add 40 ml. of sulphuric acid and make up to 100 ml. with water.

(2) *Colour Solution*—Add 35 ml. of water, 40 ml. of sulphuric acid, and 5 ml. of sodium thiocyanate solution. Make up to 100 ml. with water and stand for 15 minutes.

Measure the absorption of these two solutions using 1 cm. glass cells, Ilford Spectrum Blue-Green filters No. 603, and a water setting of 1·0. The difference between these two readings is proportional to the percentage of iron in the aluminium alloy.

CALIBRATION GRAPH

Take 1·25 grm. of H.H.P. aluminium, digest the 50 ml. of sodium hydroxide solution until the reaction ceases. Add 25 ml. of water and 25 ml. of nitric acid with due caution. Boil to complete solution and expel nitrous fumes. Cool and make up to 250 ml. with water. Take ten 20 ml. aliquots and add respectively 0, 1, 2, 3 up to 10 ml. of the H.H.P. iron solution and colour up each solution by adding 25 ml. of water, 40 ml. of sulphuric acid, and 5 ml. of sodium thiocyanate solution. Stand all solutions for 15 minutes and measure the absorptions as previously given under colour solution.

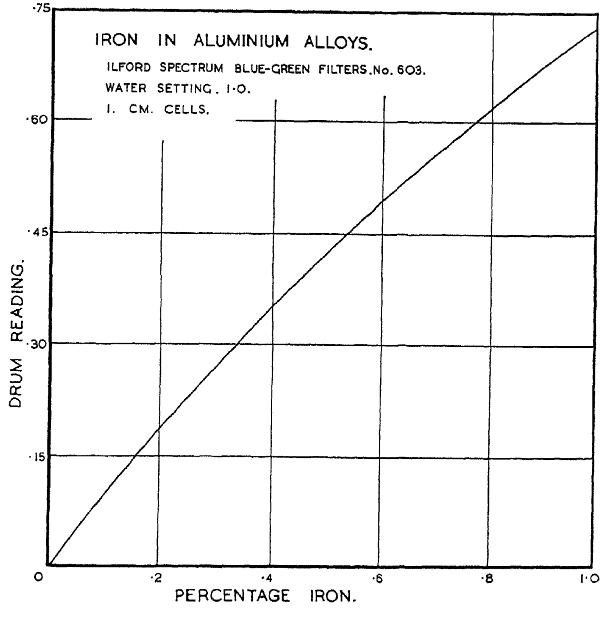


FIG. 24. Calibration graph for **IRON** in aluminium alloys.

The complete range of cells is calibrated as follows :–

Range.	Size of Cell	ml. of iron solution required.
0–2% Fe.	0·5 cm.	0, 2, 4, 6 up to 20.
0–1% Fe.	1·0 cm.	0, 1, 2, 3 up to 10.
0–0·5% Fe.	2·0 cm.	0, 0·5, 1·0, 1·5 up to 5.
0–0·25% Fe.	4·0 cm.	0, 0·25, 0·5, 0·75, 1·0 up to 2·5.

A typical calibration graph is shown in Fig. 24 using 1 cm. cells.

NOTES AND HINTS

(1) As slight fading of the iron thiocyanate may occur, it is advisable to work on a fairly strict time basis.

(2) For calibrations of 2 cm. and 4 cm. cells it is suggested that twofold and fourfold dilutions respectively of the iron solution should be employed and then 0, 1, 2, 3 up to 10 ml. of each solution is representative of the amounts cited in the table above.

(3) A blank on the reagents should be taken from time to time.

(4) The thiocyanate concentration should be controlled. Dilute 10 ml. of the solution to 200 ml. and titrate against standard N/10 silver nitrate solution. After the construction of the calibration graph subsequent titres should agree within ±2–3 per cent. of the original titre obtained.

LIMITS OF ACCURACY

This method gives an accuracy of ±2 per cent. of the iron content of the aluminium alloy.

TIME FOR ONE DETERMINATION

About 8 to 12 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 25.

(B) DIRECT METHOD

(1) Tungsten Lamp

The procedure given under (A) is followed exactly, except that the blank readings are omitted.

(2) Mercury Lamp

Precise methods have not been evolved to date using the mercury lamp, but it is probable that the same chemical procedure as outlined under (B) (1) will suffice, but that different filters will have to be used.

Determination of Manganese in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda, acidified with nitric acid, and the manganese oxidised to permanganic acid with potassium periodate.

Interference from other elements is accounted for in a similar manner as described for steels.

REAGENTS REQUIRED

Caustic soda . . .	10 per cent. solution.
Nitric acid . . .	S.G. 1·42.
Potassium periodate .	0·3 grm. solid or "Analoids."
Sodium nitrite . . .	2 per cent. solution.
Potassium permanganate	Solution standardised to contain 0·25 grm. manganese per litre.

METHOD

Take 0·5 grm. of the alloy in a 250 ml. conical beaker and dissolve in 20 ml. of caustic soda, warming if necessary until the reaction ceases. Cool, and add 10 ml. of water and 10 ml. of nitric acid, boil to complete solution and expel nitrous fumes. Add 0·3 grm. of potassium periodate, boil and maintain at boiling point for 10 minutes for complete oxidation of the manganese. Cool, and make up to 100 ml. with water. Measure the absorption of this solution, using 1 cm. glass cells and Ilford Spectrum Green filters No. 604 and a water setting of 1·0. Empty the cell, add one drop of sodium nitrite solution, fill up the cell with the original solution, and again measure the absorption of this solution as described above. The difference between the two readings is proportional to the percentage of manganese in the aluminium alloy.

CALIBRATION GRAPH

Take 1, 2, 3 up to 10 ml. of the standardised permanganate solution and to each add 20 ml. of water, 5 ml. of nitric acid, 0·3 grm. of potassium periodate, and proceed as given previously under method. Measure the absorption of these solutions using 1 cm. cells, Ilford Spectrum Green filters No. 604, and a water setting of 1·0 as described in the method. Plot the relationship between the drum difference readings and the percentage of manganese.

The complete range of cells is calibrated as follows : –

Range.	Size of Cell.	ml. of standardised $KMnO_4$ required.
0–1% Mn.	0·5 cm.	2, 4, 6 up to 20.
0–0·5% Mn.	1·0 cm.	1, 2, 3 up to 10.
0–0·25% Mn.	2·0 cm.	0·5, 1·0, 1·5 up to 5.

A typical calibration graph is shown in Fig. 13, *i.e.*, the calibration for manganese in aluminium alloys yields an identical graph to that shown for ferrous alloys, when prepared using the same Absorptiometer.

NOTES AND HINTS

(1) All dust and organic matter must be excluded.

(2) Lower ranges of manganese can be determined by using 4 cm. cells, although this is not generally required for this class of alloys.

(3) Higher ranges of manganese may be determined by dilution either of solution on a weight of 0·5 grm. or by taking an appropriately smaller weight of sample.

LIMITS OF ACCURACY

This is within ± 1 per cent. of the manganese content of the alloy.

TIME FOR ONE DETERMINATION

About 10 minutes, but only when done in batches.

REFERENCE

E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 25.

(B) DIRECT METHODS

(1) Tungsten Lamp

The procedure as given under (A) followed exactly for the direct method, omitting the blank reading.

(2) Mercury Lamp

The chemical procedure as outlined under (A) is followed exactly, except that no blank readings are required and Ilford Spectrum Yellow filters No. 606 are used.

The range covered is as follows :—

Range.	Size of Cell.
0–3·0% Mn.	0·5 cm.
0–1·5% Mn.	1·0 cm.
0–0·8% Mn.	2·0 cm.
0–0·4% Mn.	4·0 cm.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Nickel in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda and acidified with nitric acid. Aliquot portions are taken and the nickel determined as the dimethylglyoxime complex, which is formed in ammoniacal solution, precipitation being prevented by the presence of iodine. Interference from metals insoluble in ammonia is obviated by the addition of citric acid. Readings are taken which are proportional to the percentage of nickel present in the alloy.

REAGENTS REQUIRED

Caustic soda . . .	10 per cent. solution.
Nitric acid	S.G. 1·42.
Ammonium citrate .	500 grm. citric acid are dissolved in 500 ml. of ammonium hydroxide and made up to 1 litre with water.
Iodine	N/10 solution.
Ammonium hydroxide	500 ml. of ammonium hydroxide (S.G. 0·88) made up to 1 litre with water.

Ammoniacal dimethylglyoxime	1 grm. of dimethylglyoxime is dissolved in 500 ml. of ammonium hydroxide (S.G. 0·88) and made up to 1 litre with water.
Nickel	(*a*) Solution standardised to contain 0·100 grm. nickel per litre by dissolving the appropriate weight of nickel sulphate. (*b*) H.H.P. nickel.

METHOD

Take 0·5 grm. of alloy in a 250 ml. conical beaker and digest with 20 ml. of 10 per cent. caustic soda solution until the reaction ceases. Add 10 ml. of water and 10 ml. of nitric acid with due caution, boil to complete solution and expel nitrous fumes. Cool, and make up to 200 ml. with water. Take two 10 ml. aliquots and proceed as follows :

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution, and 20 ml. of ammonium hydroxide and make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of ammonium citrate solution, 35 ml. of water, 5 ml. of iodine solution, and 20 ml. of ammoniacal dimethylglyoxime and make up to 100 ml. with water.

Measure the absorption of these two solutions using 1 cm. glass cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·2. The difference between these two readings is proportional to the percentage of nickel in the aluminium alloy.

CALIBRATION GRAPH

(1) *Blank Solution* Take 10 ml. of water and 1 ml. of 10 per cent. caustic soda solution and 0·5 ml. of concentrated nitric acid and proceed as given under the blank solution above.

(2) *Colour Solution* Take 1, 2, 3 up to 10 ml. of the H.H.P. nickel solution or the standardised nickel sulphate solution and to each add 1 ml. of caustic soda solution and 0·5 ml. of nitric acid and proceed as given under the colour solution above.

Measure the absorption of each solution ; the difference in the absorptions between the colour solution and the blank plotted against the percentage nickel gives the calibration graph.

The complete range of cells is calibrated as follows:—

Range.	Size of Cell.	ml. of standardised nickel sulphate required.
0–8% Ni.	0·5 cm.	2, 4, 6 up to 20.
0–4% Ni.	1·0 cm.	1, 2, 3 up to 10.
0–2% Ni.	2·0 cm.	0·5, 1·0, 1·5 up to 5.
0–1% Ni.	4·0 cm.	0·25, 0·5, 0·75 up to 2·5.

A typical calibration graph is shown in Fig. 14, *i.e.*, the same calibration applies for aluminium alloys as ferrous alloys, using the same Absorptiometer.

NOTES AND HINTS

(1) It is very important that, both when calibrating and doing an actual determination, the blank solution should be prepared before the colour solution, thus excluding any possibility of the dimethylglyoxime being introduced into the blank solution.

(2) When obtaining a calibration graph using 4 cm. cells it is advisable to make up 50 ml. of the original nickel sulphate solution to 200 ml. with water and then to take off 1, 2, 3 up to 10 ml. of this solution for calibration.

(3) It is not advisable to leave any of these solutions in the glass cells for longer periods than is absolutely necessary as the citrate tends to stain the glass. Should this occur the cells can be cleaned with concentrated nitric acid.

(4) Higher ranges of nickel should be determined by taking a proportionately less quantity of the original alloy and not by taking a 0·5 grm. sample and diluting the final solution.

LIMITS OF ACCURACY

This method gives an accuracy of ±1 per cent. of the nickel content of the aluminium alloy.

TIME FOR ONE DETERMINATION

About 10 to 12 minutes when treated in batches.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 11.

(B) DIRECT METHODS

(1) Tungsten Lamp

The same procedure as given under (A) is adopted, omitting to take blank solutions.

(2) Mercury Lamp

The same procedure is adopted as given under (B) (1) using Ilford Spectrum Green filters No. 604 when the following ranges are obtained:

Range.	Size of Cell.
0–8% Ni.	0·5 cm.
0–4% Ni.	1·0 cm.
0–2% Ni.	2·0 cm.
0–1% Ni.	4·0 cm.

REFERENCE

E. J. Vaughan. *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, p. 44.

Determination of Silicon in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda, acidified with sulphuric acid, the dross being dissolved by the addition of bromine. The silicon is converted to silicomolybdates, and subsequently reduced by stannous chloride to molybdenum blue. The absorption of this solution is proportional to the silicon content of the alloy.

REAGENTS REQUIRED

Caustic soda	Solid.
Sulphuric acid	25 per cent. solution.
Bromine water	Saturated solution.
Ammonium molybdate	5 per cent. solution.

Stannous chloride .	Dissolve 1 grm. of stannous chloride in 1·6 ml. of concentrated hydrochloric acid and make up to 100 ml. with water. The solution used in this method is diluted by taking 10 ml. of the above solution and diluting to 200 ml. with water.
Silicate solution	Solution standardised to contain 0·02 grm. of silicon per litre. This is effected by taking 0·0428 grm. of pure silica (SiO_2) and fusing with sodium carbonate.

METHOD

Take 0·5 grm. of the alloy in a 100 ml. nickel crucible containing 2·5 grm. of solid sodium hydroxide and cautiously add 20–30 ml. of water. Allow to dissolve and maintain at incipient boiling for several minutes. Leach out into 40 ml. of 25 per cent. sulphuric acid contained in a 650 ml. conical beaker. Add 5–10 ml. of bromine water and warm to dissolve aluminium hydroxide and dross. If dross still remains, add more bromine water and swirl the beaker continuously. Boil off the excess bromine, cool, and make up to 500 ml. with water. Take two 20 ml. aliquots and treat as follows :—

(1) *Blank Solution*—Add 45 ml. of water, 10 ml. of 25 per cent. sulphuric acid, 10 ml. of ammonium molybdate, and 10 ml. of stannous chloride solution. Make up to 100 ml. with water and stand for 15 minutes.

(2) *Colour Solution*—Add 45 ml. of water and 10 ml. of ammonium molybdate and stand for 5 minutes. Add 10 ml. of 25 per cent. sulphuric acid, 10 ml. of stannous chloride, and make up to 100 ml. with water. Allow to stand for 15 minutes.

Measure the absorption of these two solutions using 1 cm. cells, Ilford Spectrum Red filters No. 608, and a water setting of 1·2.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised silicate solution and to each add 1 ml. of 25 per cent. sulphuric acid, 45 ml. of water, and 10 ml. of ammonium molybdate solution and stand for 5 minutes. Add 10 ml. of 25 per cent. sulphuric acid, 10 ml. of stannous chloride and make up to 100 ml. with water and allow to stand for 15 minutes. Measure the absorption as previously described under method and plot the relationship between drum difference readings and the percentage of silicon.

The complete range of cells is as follows :—

Range.	Size of Cell.	ml. of standardised silicate required.
0–2% Si.	0·5 cm.	0, 2, 4, 6 up to 20.
0–1% Si.	1·0 cm.	0, 1, 2, 3 up to 10.
0–0·5% Si.	2·0 cm.	0, 0·5, 1, 1·5 up to 5.

A typical calibration graph is shown in Fig. 25 using 1 cm. cells.

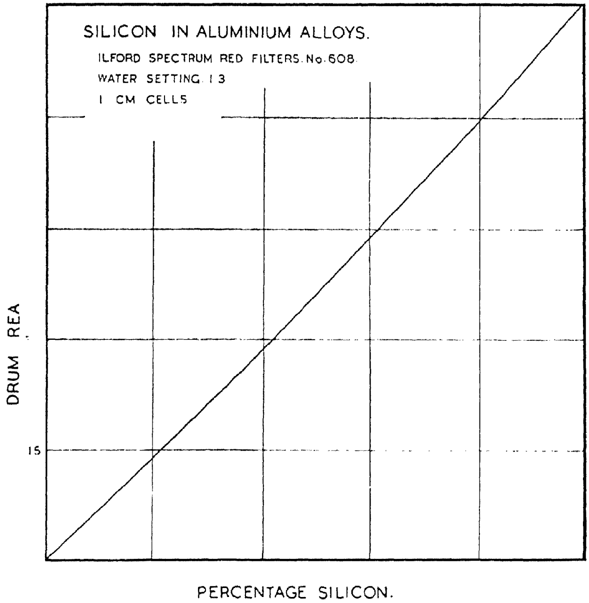


Fig. 25. Calibration graph for **SILICON** in aluminium alloys.

NOTES AND HINTS

(1) For higher concentrations of silicon there are two alternatives:

(*a*) proportionately less weight of sample;
(*b*) dilution of alloy solution;

e.g., for an alloy containing up to 15 per cent. Si take 0·125 grm. of alloy, a 10 ml. aliquot and use 0·5 cm. cells, or take 0·5 grm. of alloy, a 2·5 ml. aliquot and use 0·5 cm. cells.

(2) The reacting solutions should be made up and measured accurately.

(3) Blank determinations should be taken on all reagents from time to time.

(4) If there should be any turbidity of the solution after acidification with sulphuric acid make up to 500 ml. with water and filter off sufficient for an aliquot portion.

LIMITS OF ACCURACY

Results are within ±1 per cent. of the silicon content of the aluminium alloy.

TIME FOR ONE DETERMINATION

15 to 20 minutes when done in batches.

REFERENCES

(1) E. J. Vaughan. *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1942, pp. 11, 12, and 13.

(2) An alternative method which depends upon the absorption of the light through the yellow silico-molybdates is given in full by W. H. Hadley, *The Analyst,* vol. 67, Jan. 1942, pp. 5–8, on *The Determination of Silicon in Aluminium and its Alloys.*

(B) DIRECT METHODS

(1) Tungsten Lamp

The procedure as given under (A) is followed exactly for the direct method, omitting the blank reading.

(2) Mercury Lamp

The chemical procedure as outlined under (B) (1) is adopted using Ilford Spectrum Yellow filters No. 606. The complete range of cells is as follows:—

Range.	Size of Cell.
0–3·5% Si.	0·5 cm.
0–1·8% Si.	1·0 cm.
0–0·9% Si.	2·0 cm.
0–0·5% Si.	4·0 cm.

Determination of Titanium in Aluminium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in caustic soda, acidified with nitric acid, and to an aliquot portion sulphuric acid is added to prevent hydrolysis. The titanium is determined by the addition of hydrogen peroxide to form pertitanic acid.

REAGENTS REQUIRED

Caustic soda . . .	10 per cent. solution.
Nitric acid	S.G. 1·42.
Sulphuric acid . . .	25 per cent. solution.
Hydrogen peroxide .	10 vols.
Titanium dioxide . .	Standardised to contain 0·2 grm. titanium per litre.

METHOD

Take 1 grm. of the alloy in a 250 ml. conical beaker and dissolve by the addition of 40 ml. of caustic soda. When the reaction has ceased, add carefully 20 ml. of nitric acid and boil the aluminium hydroxide into solution. Cool, and make up to 100 ml.; take two 20 ml. aliquot portions and treat as follows:

(1) *Blank Solution.*—Add 5 ml. of sulphuric acid and make up to 50 ml. with water.

(2) *Colour Solution.*—Add 5 ml. of sulphuric acid, 5 ml. of hydrogen peroxide, and make up to 50 ml. with water.

Measure off the absorption of these solutions using 2 cm. cells, Ilford Spectrum Violet filters No. 601, and a water setting of 1·0.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised titanium solution, add 8 ml. of caustic soda and 4 ml. nitric acid to each and colour up as given under (2) above. Make each solution up to 100 ml. with water and measure off as given under (2) above.

Range	Size of Cell.	ml. of standardised titanium solution required.
0–1% Ti.	2·0 cm.	1, 2, 3 up to 10.
0–0·5% Ti.	4·0 cm.	2, 4, 6 up to 20.

A typical calibration graph is shown in Fig. 26, using 2·0 cm. cells.

NOTES AND HINTS

Care must be taken to exclude all hydrogen peroxide both in making up and measuring off the blank solution.

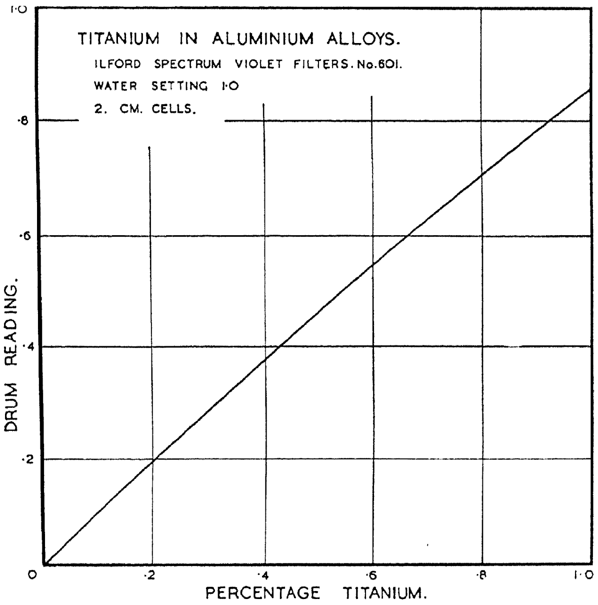


FIG. 26. Calibration graph for **TITANIUM** in aluminium alloys.

LIMITS OF ACCURACY

Results are within ±1 per cent. of the titanium content of the alloy.

TIME FOR ONE DETERMINATION

About 10 to 15 minutes when done in batches.

REFERENCE

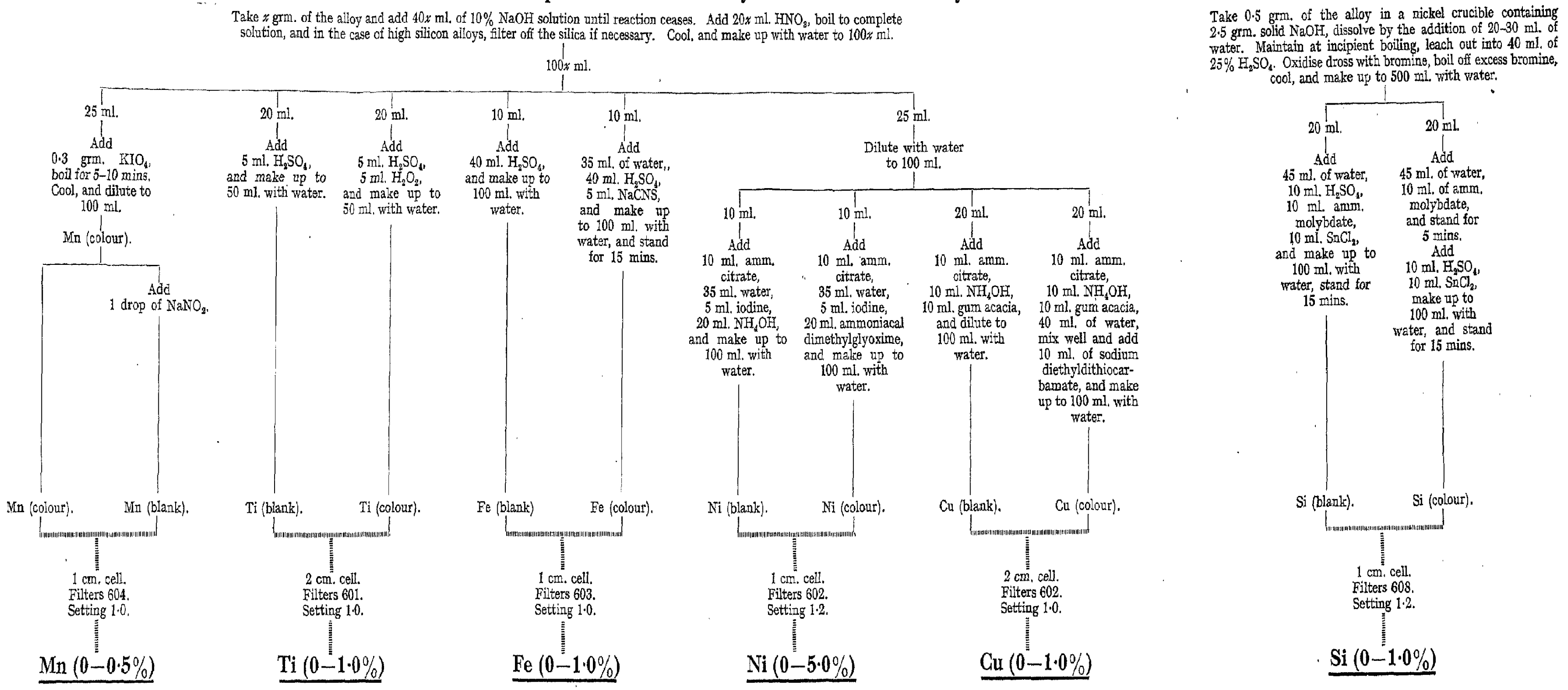
E. J. Vaughan. *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis.* Monograph published by Inst. of Chemistry, 1941, p. 25.

COMPOSITE SCHEME

ANALYSIS

ALUMINIUM ALLOYS

Composite Scheme of Analysis for Aluminium Alloys



Take x grm. of the alloy and add $40x$ ml. of 10% NaOH solution until reaction ceases. Add $20x$ ml. HNO_3, boil to complete solution, and in the case of high silicon alloys, filter off the silica if necessary. Cool, and make up with water to $100x$ ml.

$100x$ ml.

25 ml. Add 0·3 grm. KIO_4, *boil for 5–10 mins.* Cool, and dilute to 100 ml.
Mn (colour).
Add 1 drop of $NaNO_2$.
Mn (colour). Mn (blank).
1 cm. cell. Filters 604. Setting 1·0.
Mn (0–0·5%)

20 ml. Add 5 ml. H_2SO_4, *and make up to* 50 ml. with water.
5 ml. 20 ml. Add 5 ml. H_2SO_4, *5 ml.* H_2O_2, and make up to 50 ml. with water.
Ti (blank). Ti (colour).
2 cm. cell. Filters 601. Setting 1·0.
Ti (0–1·0%)

10 ml. Add 40 ml. H_2SO_4, and make up to 100 ml. with water.
10 ml. Add 35 ml. of water,, *40 ml.* H_2SO_4, 5 ml. NaCNS, and make up to 100 ml. with water, and stand for 15 mins.
Fe (blank) Fe (colour).
1 cm. cell. Filters 603. Setting 1·0.
Fe (0–1·0%)

25 ml. Dilute with water to 100 ml.

10 ml. Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. NH_4OH, and make up to 100 ml. with water.
10 ml. Add 10 ml. amm. citrate, 35 ml. water, 5 ml. iodine, 20 ml. ammoniacal dimethylglyoxime, and make up to 100 ml. with water.
Ni (blank). Ni (colour).
1 cm. cell. Filters 602. Setting 1·2.
Ni (0–5·0%)

20 ml. Add 10 ml. amm. citrate, 10 ml. NH_4OH, 10 ml. gum acacia, and dilute to 100 ml. with water.
20 ml. Add 10 ml. amm. citrate, 10 ml. NH_4OH, 10 ml. gum acacia, 40 ml. of water, mix well and add 10 ml. of sodium diethyldithiocarbamate, and make up to 100 ml. with water.
Cu (blank). Cu (colour).
2 cm. cell. Filters 602. Setting 1·0.
Cu (0–1·0%)

Take 0·5 grm. of the alloy in a nickel crucible containing 2·5 grm. solid NaOH, dissolve by the addition of 20–30 ml. of water. Maintain at incipient boiling, leach out into 40 ml. of 25% H_2SO_4. Oxidise dross with bromine, boil off excess bromine, cool, and make up to 500 ml. with water.

20 ml. Add 45 ml. of water, 10 ml. H_2SO_4, 10 ml. amm. molybdate, 10 ml. $SnCl_2$, and make up to 100 ml. with water, stand for 15 mins.
20 ml. Add 45 ml. of water, 10 ml. of amm. molybdate, and stand for 5 mins. Add 10 ml. H_2SO_4, 10 ml. $SnCl_2$, make up to 100 ml. with water, and stand for 15 mins.
Si (blank). Si (colour).
1 cm. cell. Filters 608. Setting 1·2.
Si (0–1·0%)

(B) DIRECT METHOD

Tungsten Lamp

The same procedure is carried out as given under (A), except that blank readings are omitted.

Composite Scheme of Analysis for Aluminium Alloys

It will be seen from the methods already given under aluminium alloys that the alloy is always dissolved initially in caustic soda. Accordingly a composite scheme has been worked out for these alloys which is shown in Fig. 27. It is not always required to carry out all the determinations given under the ranges specified and methods must be adjusted accordingly.

CHAPTER VIII

MAGNESIUM ALLOYS

THE determinations given are for the following elements in commercial magnesium alloys:—Aluminium, Copper, Iron, Manganese, and Silicon.

In every case given it is advisable to use only the best analytical reagents obtainable.

With magnesium alloys it is nearly always possible to apply direct methods, because the amounts of interfering elements, other than aluminium, are small. On the other hand, due to this fact, it is essential to take periodic checks on the reagents used.

Determination of Aluminium in Magnesium Alloys

(A) DIFFERENCE METHOD

Difference methods are not applicable to this determination.

(B) DIRECT METHODS

(1) Tungsten Lamp

The alloy is dissolved in acetic acid solution, thereby providing an automatically buffered solution. Aliquots are coloured up with alizarin S solution. Other metals producing colours with alizarin S namely, iron and copper—are not present in sufficient quantities to cause interference.

REAGENTS REQUIRED

Acetic acid . . .	33 per cent. solution.
Alizarin S . . .	0·25 per cent. solution in water.
Magnesium alloy .	Containing a known percentage of aluminium over the range required.

METHOD

Take 0·1 grm. of the alloy in a 400 ml. conical beaker, cover with 10 ml. of water, add 5 ml. of acetic acid solution and allow to dissolve. When the reaction ceases add 100 ml. of water and warm at 50–60° C., maintaining at this temperature for 15 to 30 minutes in order to dissolve the dross. Cool, make up to 200 ml. with water.

For aluminium contents up to 6 per cent. take 20 ml.

For aluminium contents up to 12 per cent. take 10 ml.

Place the aliquot in a 200 ml. volumetric flask, add 100 ml. of water, 10 ml. of alizarin S solution and dilute to the mark with water. Allow to stand for 15 to 30 minutes and measure the absorption of these solutions using 1 cm. glass cells, Ilford Spectrum Blue-Green filters No. 603, and a water setting of 1·0. The reading obtained is proportional to the percentage of aluminium in the magnesium alloy.

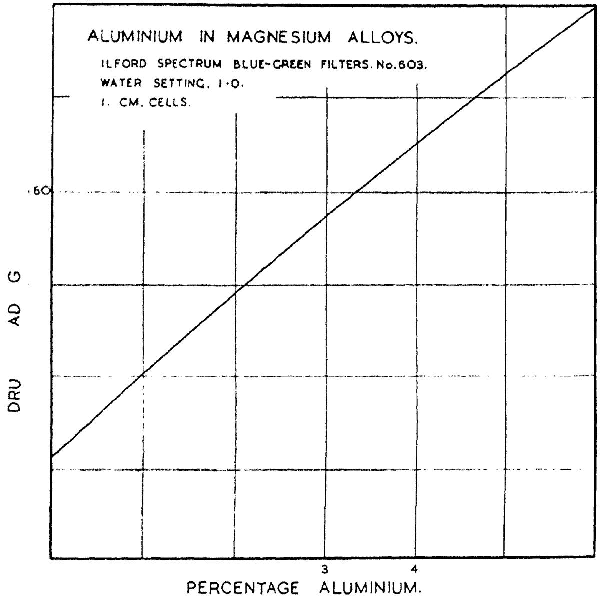


FIG. 28. Calibration graph for **ALUMINIUM** in magnesium alloys.

CALIBRATION GRAPH

Take 0·1 grm. of the standard magnesium alloy, dissolve and make up as described above under method. Take aliquot portions to represent 0, 0·5, 1·0, 1·5 up to 6·0 per cent. of aluminium. Colour up and measure the absorption of these solutions as described previously, and construct a graph showing the relationship between drum readings and percentage of aluminium.

A typical calibration graph using 1 cm. glass cells and Ilford Spectrum Blue-Green filters No. 603 is shown in Fig. 28.

NOTES AND HINTS

(1) If the percentage of zinc in the magnesium alloy is high, complete solution is not effected but all the aluminium is dissolved.

(2) The colour should be allowed to develop within a temperature range of 5° C.

(3) The quantity of the aliquot taken may be varied according to the range required—for example, an alloy containing 3 per cent. of aluminium may be determined by making up to 100 ml. instead of the normal 200 ml. and taking a 20 ml. aliquot.

(4) An alternative calibration graph can be prepared over the range 0–5 per cent. using 2 cm. cells and a water setting of 1·3.

(5) As different supplies of alizarin S have very slightly different characteristics a fairly large supply of this reagent from one source should be obtained (250 grm. should suffice for 10,000 determinations). If a new source of supply is necessitated recalibration must be carried out.

LIMITS OF ACCURACY

An accuracy of ±1 per cent. of the aluminium content of the magnesium alloy is obtained.

TIME FOR ONE DETERMINATION

5 to 10 minutes when treated in batches.

REFERENCE

F. W. Haywood, F. Harrison, and A. A. R. Wood. *Journ. Soc. Chem. Ind.*, vol. 62, No. 11, November 1943, pp. 187–189.

(2) Mercury Lamp

Suitable light selectivity cannot be obtained using this lamp.

Determination of Copper in Magnesium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in sulphuric acid, oxidised with hydrogen peroxide and copper determined by the formation of the diethyldithiocarbamate complex in ammoniacal solution. Metals insoluble in ammonia are held in solution by the use of citric acid.

REAGENTS REQUIRED

Sulphuric acid . .	15 per cent. solution.
Hydrogen peroxide	10 vols.
Ammonium citrate	500 ml. of ammonium hydroxide (S.G. 0·88) is added to 500 grm. of citric acid until solution is complete, and made up to 1 litre with water.
Ammonium hydroxide	200 ml. of ammonium hydroxide (S.G. 0·88) is made up to 1 litre with water.
Colloid	1·0 grm. of gum acacia is dissolved in 100 ml. of hot water and the solution made up to 200 ml. with water.
Sodium diethyldithiocarbamate . .	0·50 grm. is made up to 250 ml. with water.
Copper	H.H.P. copper.

METHOD

(*a*) Copper percentage 0–0·5%

Take 1·0 grm. of the alloy in a 250 ml. conical beaker, cover with 40 ml. of water and add 20 ml. of sulphuric acid. Allow to dissolve, warming if necessary, and when the reaction ceases add 3–5 ml. of hydrogen peroxide. Boil until the dross is dissolved and a clear solution obtained. Cool, and make up to 100 ml. with water. Take two 10 ml. aliquots and proceed as follows :—

(1) *Blank Solution*—Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide, 10 ml. of gum acacia, and make up to 100 ml. with water.

(2) *Colour Solution* Add 10 ml. of ammonium citrate solution, 10 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and 40 ml. of water. Shake well and then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up the volume to 100 ml. with water.

Measure the absorption of these solutions using 2 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The difference between (1) and (2) represents the colour due to copper and is read from the appropriate calibration graph.

(*b*) Copper percentage 0–0·10%

The alloy sample of weight 1·0 grm. is dissolved and made up as described under method (A). Take two 25 ml. aliquot portions and proceed as follows :

(1) *Blank Solution* Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and make up to 100 ml. with water.

(2) *Colour Solution*—Add 20 ml. of ammonium citrate solution, 20 ml. of ammonium hydroxide, 10 ml. of gum acacia solution, and shake well; then add 10 ml. of sodium diethyldithiocarbamate solution, and finally make up to 100 ml. with water.

Measure the absorption of these solutions by means of 4 cm. cells, Ilford Spectrum Blue filters No. 602, and a water setting of 1·0. The difference between (1) and (2) represents the colour due to copper.

CALIBRATION GRAPH

(*a*) Copper percentage 0–0·5%

Take 0·50 grm. of H.H.P. copper and dissolve in 10 ml. of nitric acid (S.G. 1·42), boil to expel nitrous fumes and make up to 1 litre with water. Take 50 ml. of this solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution, and to each volume add 2 ml. of sulphuric acid and colour up the solution as previously described under (A) (2). At the same time carry out a blank estimation of the normal reagents used, that is excluding the copper solution, and check these periodically. The absorption of these solutions is measured on the Absorptiometer with 2 cm. cells as described previously.

(*b*) Copper percentage 0–0·10%

Take 25 ml. of the original copper solution and dilute with water to 500 ml. Burette off 1, 2, 3 up to 10 ml. of this solution, and to each volume add 4 ml. of sulphuric acid solution and colour up these solutions as previously described under this heading. A corresponding blank determination must be carried out and the solutions checked periodically. The absorption of these solutions is measured with 4 cm. cells, as described under (*b*) (2).

A typical calibration graph is shown in Fig. 29 using 2 cm. cells.

NOTES AND HINTS

(1) When calibrating and during an actual determination, it is important that the blank solution be prepared before the colour solution.

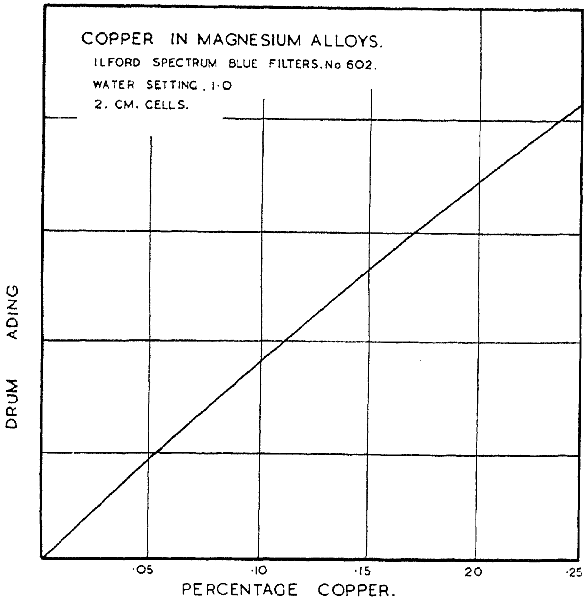
(2) It is not advisable to leave any of the solution in the glass cells longer than necessary as the citrate tends to stain the glass.

This may be removed by leaving the cells soaking overnight in nitric acid (S.G. 1·42).

(3) Instead of adding 3·5 ml. of H_2O_2, 0·5 grm. of Na_2O_2 may be used. If silicon is absent from the alloy, oxidation may be effected by adding a few drops of HNO_3 (S.G. 1·42).

LIMITS OF ACCURACY

An accuracy of ± 1 per cent. of the copper content of the magnesium alloy is obtained.



G. 29. Calibration graph for **COPPER** in magnesium alloys.

TIME FOR ONE DETERMINATION

10 to 15 minutes when treated in batches.

REFERENCE

F. W. Haywood and A. A. R. Wood. Adaptation of method described in *The Analyst*, vol. 68, July 1943, pp. 206–208.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure as described under (A) is carried out, omitting to take blank readings.

(2) Mercury Lamp

The same chemical procedure as used in (A) is adopted, but using filters, namely Chance No. 6 and Wratten No. 50. Under such conditions the range covered for method (*a*) is as follows :

Range.	Size of Cell.
0–0·3% Cu.	2 cm.
0–0·15% Cu.	4 cm.

Determination of Iron in Magnesium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

Solution of the alloy is effected in sulphuric acid and after oxidation with hydrogen peroxide the iron is coloured up by the thiocyanate reaction.

REAGENTS REQUIRED

Sulphuric acid . . .	15 per cent. solution.
Hydrogen peroxide .	10 vols.
Sodium thiocyanate	20 per cent. solution.
Iron	H.H.P. iron. Take 0·25 grm. iron and dissolve in a minimum quantity of sulphuric acid and make up to 1 litre with water. Take 50 ml. of this solution and dilute to 500 ml. with water.
Magnesium . .	H.H.P. magnesium.

METHOD

Take 1 grm. of the alloy in a 250 ml. conical beaker, cover with 40 ml. of water and add 20 ml. of sulphuric acid. Allow to dissolve, warming if necessary, and when the reaction ceases add 3–5 ml. of hydrogen peroxide. Boil until the dross is dissolved and a clear solution obtained; cool and make up to 100 ml. with water. Take two 50 ml. aliquot portions and treat as follows:

(1) *Blank Solution*—Make up to 100 ml. with water.

(2) *Colour Solution*—Add 10 ml. of sodium thiocyanate and make up to 100 ml. with water.

Measure the absorptions of (1) and (2) using Ilford Spectrum Blue-Green filters No. 603, 4 cm. cells, and a water setting of 1·0. The difference between these two readings is proportional to the percentage of iron in the alloy.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the H.H.P. iron solution and to each add 0·5 grm. of H.H.P. magnesium. Cover with 40 ml. of water and add 10 ml. of sulphuric acid. Allow to dissolve, warming if necessary, and when the reaction ceases add 3–5 ml. of hydrogen peroxide. Boil until the dross is dissolved and a clear solution obtained; cool, add 10 ml. of sodium thiocyanate and make up to 100 ml. with water. Measure the absorption of these solutions as given under method and construct a graph showing the relationship between drum difference readings and percentage of iron.

The range obtained is as follows:—

Range.	Size of Cell.	ml. of standardised iron.
0–0·1% Fe.	2 cm.	0, 2, 4, 6 up to 20.
0–0·05% Fe.	4 cm.	0, 1, 2, 3 up to 10.

A typical calibration graph using 4 cm. cells is shown in Fig. 30.

NOTES AND HINTS

(1) As slight fading of the iron thiocyanate may occur it is advisable to work on a fairly strict time basis.

(2) A blank on the reagents should be taken from time to time.

(3) The concentration of the thiocyanate solution should be controlled by diluting 10 ml. of the original solution to 200 ml. with water and titrating against N/10 silver nitrate solution. The titre should be within 2–3 per cent. of the reading taken when obtaining the original calibration graph.

(4) 0·5 grm. of Na_2O_2 may be added instead of the 3–5 ml. of H_2O_2. In the absence of silicon in the alloy, oxidation may be effected by adding a few drops of HNO_3 (S.G. 1·42).

LIMITS OF ACCURACY

This method gives an accuracy of ±2 per cent. of the iron content of the magnesium alloy.

TIME FOR ONE DETERMINATION

About 8 to 10 minutes when done in batches.

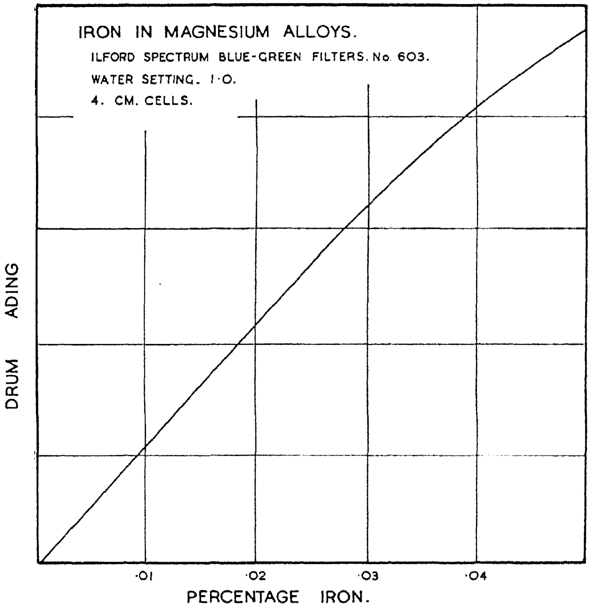


FIG. 30. Calibration graph for **IRON** in magnesium alloys.

(B) DIRECT METHOD

(1) Tungsten Lamp

The same procedure as outlined in (A) is adopted, omitting to take blank readings.

(2) Mercury Lamp

The same chemical procedure as used in (A) is adopted, but using filters Chance No. 6 and Wratten No. 50. The range thus obtained is the same as given under (A).

Determination of Manganese in Magnesium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in sulphuric acid and the manganese oxidised by the silver persulphate reaction to permanganic acid. Interference from other elements producing colours is obviated by decolorising the permanganic acid with sodium nitrite solution.

REAGENTS REQUIRED

Sulphuric acid . . .	15 per cent. solution.
Hydrogen peroxide .	10 vols.
Silver nitrate . . .	2 per cent. solution.
Ammonium persulphate	2·5 grm. solid or " Analoids."
Urea	0·5 grm. solid or " Analoids."
Sodium nitrite . . .	2 per cent. solution.
Potassium permanganate	Solution standardised to contain 0·25 grm. manganese per litre.

METHOD

Take 0·5 grm. of the alloy in a 250 ml. conical beaker and dissolve in 20 ml. of sulphuric acid. When the reaction ceases, add 3–5 ml. of hydrogen peroxide and boil to complete solution. Cool and make up to about 50 ml. with water. Add 10 ml. of 2 per cent. silver nitrate solution and 2·5 grm. of ammonium persulphate. Boil until the evolution of oxygen is complete, and cool. Add 0·5 grm. of urea and make the solution up to 100 ml. with water. Measure the absorption of this solution using a 1 cm. cell, Ilford Spectrum Green filters No. 604, and a water setting of 1·0. Empty the cell, add one drop of sodium nitrite solution, fill up the cell with the original solution and again measure the absorption of this solution as previously described. The difference between these two readings is proportional to the percentage of manganese in the alloy.

CALIBRATION GRAPH

Take 1, 2, 3 up to 10 ml. of the standardised permanganate solution and to each add 20 ml. of water and 10 ml. of sulphuric acid; add silver nitrate and ammonium persulphate and proceed as stated previously under method. Measure the absorption of these solutions in 1 cm. cells. Plot a graph showing the relationship between difference drum divisions and percentage manganese.

The complete range of cells is calibrated as follows :

Range.	Size of Cell.	ml. of $KMnO_4$ solution required.
0-1% Mn.	0·5 cm.	2, 4, 6 up to 20.
0-0·5% Mn.	1·0 cm.	1, 2, 3 up to 10.
0-0·25% Mn.	2·0 cm.	0·5, 1·0, 1·5 up to 5.

A typical calibration graph is that shown in Fig. 13, using 1 cm. cells. The graph for manganese in ferrous alloys is identical to that for manganese in magnesium alloys when employing the same Absorptiometer.

NOTES AND HINTS

(1) When reducing the permanganic acid with sodium nitrite the urea reacts with the latter to produce small bubbles of nitrogen, which, if the cells are not scrupulously clean, adhere to the sides of the cell and give inaccurate readings. The cure for this is perfectly clean cells.

(2) Dust and organic matter must be excluded.

(3) Higher ranges of manganese may be determined by dilution either of the solution on a weight of 0·5 grm. or by taking an appropriately smaller weight of sample.

(4) 0·5 grm. of Na_2O_2 may be added instead of 3·5 ml. of H_2O_2. In the absence of silicon in the alloy, oxidation may be effected by the addition of a few drops of HNO_3 (S.G. 1·42).

LIMITS OF ACCURACY

This method gives an accuracy of ± 1 per cent. of the manganese content of the alloy.

TIME FOR ONE DETERMINATION

About 10 minutes when treated in batches.

(B) DIRECT METHOD

(1) Tungsten Lamp

The procedure as given under (A) is followed exactly for the direct method, omitting the blank reading.

(2) Mercury Lamp

The chemical procedure as outlined under (A) is followed exactly, except that no blank readings are required, and Ilford Spectrum Yellow filters No. 606 are used.

The range covered is as follows:—

Range.	Size of Cell.
0–3·0% Mn.	0·5 cm.
0–1·5% Mn.	1·0 cm.
0–0·8% Mn.	2·0 cm.
0–0·4% Mn.	4·0 cm.

Determination of Silicon in Magnesium Alloys

(A) DIFFERENCE METHOD

Tungsten Lamp

The alloy is dissolved in a minimum quantity of sulphuric acid and the silicon converted to silico-molybdates, which are subsequently reduced by stannous chloride to molybdenum blue. The absorption of this solution is proportional to the silicon content of the alloy.

REAGENTS REQUIRED

Sulphuric acid . . .	15 per cent. solution.
Hydrogen peroxide .	10 vols.
Ammonium molybdate	5 per cent. solution.
Sulphuric acid .	25 per cent. solution.
Stannous chloride	Dissolve 1 grm. of stannous chloride in 1·6 ml. of concentrated hydrochloric acid and make up to 100 ml. with water. The solution used in this method is obtained by taking 10 ml. of the above solution and diluting to 200 ml. with water.
Silicate solution	Solution standardised to contain 0·02 grm. of silicon per litre. This is effected by taking 0·0428 grm. of pure silica (SiO_2) and fusing with sodium carbonate.

METHOD

Take 1 grm. of the alloy in a 250 ml. conical beaker, cover with 40 ml. of water and add 20 ml. of 15 per cent. sulphuric acid. Allow to dissolve, warming if necessary, and when the reaction ceases, add 3–5 ml. hydrogen peroxide. Boil until the dross is dissolved and a clear solution obtained; cool, and make up to 100 ml. with water. Take two 10 ml. aliquot portions and proceed as follows:—

(1) *Blank Solution*—Add 45 ml. of water, 10 ml. of 25% sulphuric acid, 10 ml. of ammonium molybdate, and 10 ml. of stannous chloride solution. Make up to 100 ml. with water and stand for 15 minutes.

(2) *Colour Solution*—Add 45 ml. of water and 10 ml. of ammonium molybdate and stand for 5 minutes. Add 10 ml. of 25 per cent. sulphuric acid, 10 ml. of stannous chloride, and make up to 100 ml. with water. Allow to stand for 15 minutes.

Measure the absorption of these two solutions using 1 cm. cells, Ilford Spectrum Red filters No. 608, and a water setting of 1·2.

CALIBRATION GRAPH

Take 0, 1, 2, 3 up to 10 ml. of the standardised silicate solution and to each add 1 ml. of 25 per cent. sulphuric acid, 45 ml. of water, and 10 ml. of ammonium molybdate solution and stand for 5 minutes. Add 10 ml. of 25 per cent. sulphuric acid, 10 ml. of stannous chloride and make up to 100 ml. with water, and allow to stand for 15 minutes. Measure the absorption as previously described under method and plot the relationship between drum difference readings against the percentage of silicon.

The complete range of cells is as follows:—

Range.	Size of Cell.	ml. of standardised silicate solution required.
0–0·3% Si.	0·5 cm.	0, 2, 4, 6 up to 20.
0–0·15% Si.	1·0 cm.	0, 1, 2, 3 up to 10.

A typical calibration graph is shown in Fig. 31 using 1 cm. cells.

NOTES AND HINTS

(1) For higher concentrations of silicon there are two alternatives:
    (*a*) proportionately less weight of sample;
    (*b*) dilution of alloy solution.

(2) The reacting solutions should be made up and measured accurately.

(3) Blank determinations should be taken on all reagents from time to time.

(4) Instead of adding 3·5 ml. of H_2O_2 after dissolution in H_2SO_4, 0·5 grm. of Na_2O_2 may be used for oxidation.

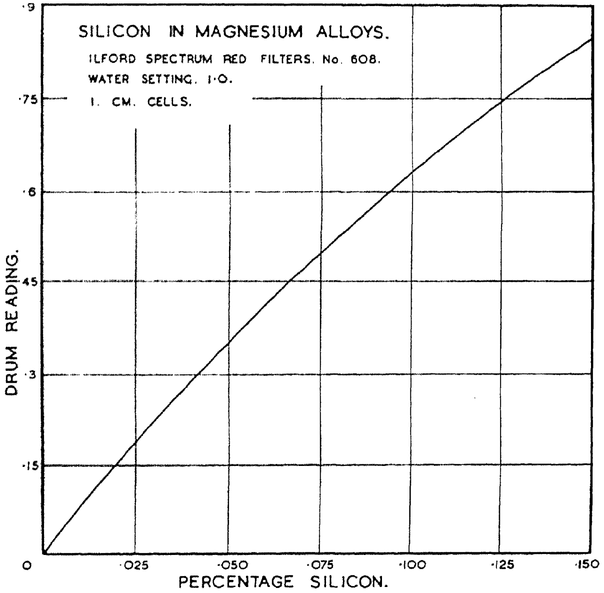


Fig. 31. Calibration graph for **SILICON** in magnesium alloys.

LIMITS OF ACCURACY

Results are within ± 1 per cent. of the silicon content of the magnesium alloy.

TIME FOR ONE DETERMINATION

15 to 20 minutes when done in batches.

REFERENCE

Adaptation of Vaughan's method for silicon in aluminium alloys, *vide* pp. 103–106. By F. Harrison (private communication).

(B) DIRECT METHOD

(1) Tungsten Lamp

The procedure as given under (A) is followed exactly for the direct method, omitting the blank reading.

(2) Mercury Lamp

The chemical procedure as outlined under (B) (1) is adopted using Ilford Spectrum Yellow filters No. 606. The range obtained is as follows :—

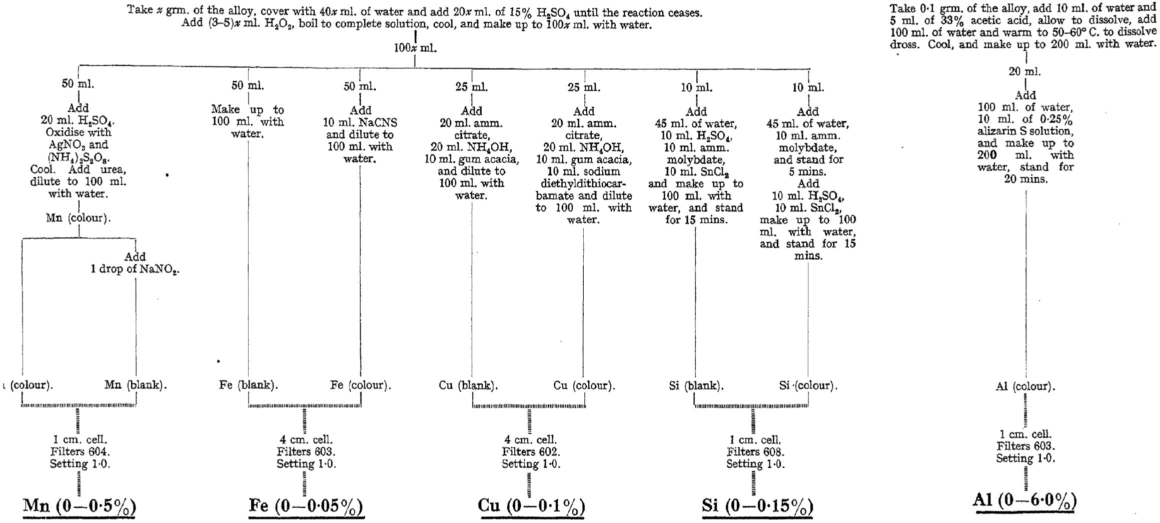
Range.	Size of Cell.
0–0·45% Si.	1·0 cm.
0–0·1% Si.	4·0 cm.

Composite Scheme of Analysis for Magnesium Alloys

A composite scheme of analysis on lines similar to that given for ferrous, copper, and aluminium alloys has been evolved for magnesium alloys, see Fig. 32. The initial solution is obtained in sulphuric acid for all the elements cited except aluminium.

As a general rule the methods given fit in with the normal ranges encountered in magnesium alloys used in industry to-day.

Composite Scheme of Analysis for Magnesium Alloys



Take x grm. of the alloy, cover with $40x$ ml. of water and add $20x$ ml. of 15% H_2SO_4 until the reaction ceases. Add $(3\text{–}5)x$ ml. H_2O_2, boil to complete solution, cool, and make up to $100x$ ml. with water.

$100x$ ml.

50 ml. Add 20 ml. H_2SO_4. Oxidise with $AgNO_3$ and $(NH_4)_2S_2O_8$. Cool. Add urea, dilute to 100 ml. with water.

Mn (colour).

(colour).

Add 1 drop of $NaNO_2$. Mn (blank).

1 cm. cell. Filters 604. Setting 1·0.

Mn (0—0·5%)

50 ml. Make up to 100 ml. with water. Fe (blank).

50 ml. Add 10 ml. NaCNS and dilute to 100 ml. with water. Fe (colour).

4 cm. cell. Filters 603. Setting 1·0.

Fe (0—0·05%)

25 ml. Add 20 ml. amm. citrate, 20 ml. NH_4OH, 10 ml. gum acacia, and dilute to 100 ml. with water. Cu (blank).

25 ml. Add 20 ml. amm. citrate, 20 ml. NH_4OH, 10 ml. gum acacia, 10 ml. sodium diethyldithiocarbamate and dilute to 100 ml. with water. Cu (colour).

4 cm. cell. Filters 602. Setting 1·0.

Cu (0—0·1%)

10 ml. Add 45 ml. of water, 10 ml. H_2SO_4, 10 ml. amm. molybdate, 10 ml. $SnCl_2$ and make up to 100 ml. with water, and stand for 15 mins. Si (blank).

10 ml. Add 45 ml. of water, 10 ml. amm. molybdate, and stand for 5 mins. Add 10 ml. H_2SO_4, 10 ml. $SnCl_2$, make up to 100 ml. with water, and stand for 15 mins. Si (colour).

1 cm. cell. Filters 608. Setting 1·0.

Si (0—0·15%)

Take 0·1 grm. of the alloy, add 10 ml. of water and 5 ml. of 33% acetic acid, allow to dissolve, add 100 ml. of water and warm to 50–60° C. to dissolve dross. Cool, and make up to 200 ml. with water.

20 ml. Add 100 ml. of water, 10 ml. of 0·25% alizarin S solution, and make up to 200 ml. with water, stand for 20 mins. Al (colour).

1 cm. cell. Filters 603. Setting 1·0.

Al (0—6·0%)

COMPOSITE SCHEME

of

ANALYSIS

Al, Cu, Fe, Mn, and Si

in

MAGNESIUM ALLOYS

Fig. 32

NAME INDEX

Allsopp, C. B., 37

Beer, 3, 4
Bolsover, G. R., 71
British Aluminium Co., Ltd., 37
B. D. H., Ltd., 37
Bunsen, 3

Eggertz, 2

Feigh, F., 37
Fox, Samuel, & Co., Ltd., 71

Hadley, W. H., 106
Harrison, F., 112, 123
Haywood, F. W., 49, 54, 94, 112, 115
Hilger, Adam, Ltd., 22
Hopkins and Williams, Ltd., 37

Keates, 1

Lambert, 2
Lampadius, 1
Lothian, G. F., 32

Matthews, J. W., 37
Mellan, I., 37

Nessler, 1

Ossian, 1

Ridsdale, N. D., & Co., Ltd., 61
Roscoe, 3

Snell, E. D. and C. R., 37

Twyman, F., VI., 32, 37

Vaughan, E. J., 29, 36, 43, 46, 56, 57, 61, 64, 65, 67, 68, 73, 74, 82, 84, 87, 91, 97, 99, 100, 102, 103, 106, 108, 123

Wild Barfield Electric Furnaces, Ltd., 78, 87
Wood, A. A. R., 49, 54, 94, 112, 115

Yoe, 37

Zeiss, Carl, 4, 37

SUBJECT INDEX

ting, 17
ges of, 29
  best range of readings, 32
  calibration of, 20
  cleaning of,
  conversion tables for, 23
  direct reading with, 19
  effect of stray light on, 12
  electrical connections of,
  location of, 12
  operation of, 12
  sensitivity adjustment, 17
  setting, 16
  setting for routine metallurgical analyses, 18
  Spekker Photo-electric, 4, 6
    principle of, 6
  " water-to-water " setting of, 17
  working cabinet for, 12
Absorptiometric Analysis (see under separate substances)
    accuracy of, 32, 43, 46, 49, 54, 56, 61, 64, 67, 71, 72, 78, 79, 82, 84, 87, 90, 94, 97, 99, 102, 106, 108, 112, 115, 118, 120, 123
Absorptiometric Analysis, accuracy
      effect of drum reading on, 32
      in relation to concentration, 34
      optimum density for, 32
    advantages of, 29
    difference methods, 39 (see under individual substances)
    direct methods, 39 (see under individual substances)
    extension of range, 30
    future developments of, 35
    limitations of, 35
    suggested apparatus for, 34
    time taken in, 34, 43, 46, 49, 54, 56, 61, 64, 67, 71, 73, 78, 79, 82, 84, 87, 91, 94, 97, 99, 102, 106, 108, 112, 115, 118, 120, 123
Absorption, coefficient, 2
  laws and definitions of, 2
  of coloured solutions, 8
Alloys, standard, 35
Aluminium Alloys, Analysis of, 30, 92 *et seq.*
      composite scheme, 109
    determination of copper in, 92
      iron in, 95
      manganese in, 98
      nickel in, 100
      silicon in, 103
      titanium in, 107
  bronze, manganese in, 82
  in magnesium alloys, 110
Ammonia, Nessler's analysis for, 1
Analysis, composite schemes of (see also under separate substances), 29
Aspirators, 35

B

Beakers for absorptiometry, 34
  nickel and silver, 35
Beer's Law, 2, 4, 30
    departure from, 4
Bibliography, 36
Blank reading, 20
    for reagents, 27
Bottles, dropping, 35
Brass analysis, 78
    copper in, 78
    iron in, 26, 79
    manganese in, 82
Bronze analysis, 76, 78, 79
    copper in, 78
    manganese in, 82
Burettes, 35

C

Calibrated glassware, 26
Calibration (see also under separate substances)
  for different cell lengths, 31
  graph, 21
    conversion tables from, 23
    periodical check of, 21
    not cutting zero, 25
  of absorptiometers, 21
  of colorimeters, 20
  time and temperature effects in, 26
Carbon in steel, Eggertz's Method for, 2
Cast iron, 40
Cells for liquids, 6
      citrate staining of, 53, 64, 86, 94, 102, 114
      cleanliness of, 26, 28
      flow-through, 28
      pickling bath for, 28
      sizes of, 27
      stannous chloride staining of, 60
      use of different sizes, 30
      use of, 28
Chance " Calorex " filters, 9
Chance filters, 11
Chemicals, 35
Choke for mercury vapour lamp, 14
Chromium in Ferrous Alloys, 41, 43
Citrate staining of cells, 53, 64, 86, 94, 102, 114
Cobalt in Ferrous Alloys, 47
Colorimeters, 1, 4

Colorimetric Analysis
  Calibration, 20
    by Balancing, 20
      Dilution, 21
      Duplication, 21
      Standard Series, 21
  general principles, 1, 20
  interfering elements in, 1
  Keates' method for copper, 1
  Lampadius' method for cobalt, 1
  of ammonia, 1
  Ossian's method for iron, 1
  reagents for, 2
Colour Filters (see filters)
Composite schemes of analysis, 29
  for aluminium alloys, 109
  for copper alloys, 91
  for ferrous alloys, 74
  for magnesium alloys, 124
Concentration of solutions, 31
Conversion tables, 23
Copper Alloys, analysis of, 30
  composite analysis of, 87, 91
  determining copper in, 76
    iron in, 26, 79
    manganese in, 82
    nickel in, 85
    phosphorus in, 87
 cuprammonium compound test, 2
 diethyldithiocarbamate complex, 9
    choice of filters for, 9
 in aluminium alloys, 92
 in brasses, 76
 in copper alloys, 76
 in ferrous alloys, 50
 in magnesium alloys, 112
Correction graphs, 25
Cupro-nickel alloys, 78, 79
    iron in, 79
    manganese in, 82
Cylinders, graduated, 35

D

Density, 4
Dilution of solutions, 30, 32
    table of available methods, 33
Direct readings on Spekker Absorptiometer, 19
Dropping bottles, 35

E

Extinction Coefficient, 3
  molecular, 3

    Alloys, analysis of, 29, 39
    chromium in, 41, 43
    cobalt in, 47
    composite scheme, 74

Ferrous Alloys, analysis of
    copper scheme, 50
    manganese, 55
    molybdenum, 57
    nickel, 62
    silicon, 65
    titanium, 68
    vanadium, 71
Filters, 6
 Chance, 11
 choice of, 9, 39
 choice to compensate concentration, 32
 effect on sensitivity of Absorptiometer, 9
 for mercury vapour lamp, 11
 heat absorbing, 9
 Ilford, 9
   transmission data for, 10
 need for, 8
 Wood's Glass, 11
 Wratten, 11
Flask, volumetric, 35

G

Graduated cylinders, 35
Graphs, calibration, 21
 correction, 25
Gun metal, determination of iron in, 79
    manganese in, 82

H

Heat absorbing filters, 9
H. H. P. metals, 22
High speed steels, 40
    substitute "66," molybdenum in, 56
 chromium steels, manganese in, 56

I

Ilford Spectrum Filters, 9
    transmission data, 10
Interfering elements, difference method, 19
Iris diaphragm, 7
Iron in aluminium alloys, 95
   copper alloys, 26
   magnesium alloys, 116

L

Lambert's Law, 2, 30
Light sources, 6, 8
   fitting, 14
Literature, 36

M

Magnesium Alloys, analysis of, 30, 110
    Composite, 124
  aluminium in, 110
  copper in, 112
  iron in, 116

Magnesium Alloys, analysis of
    manganese in, 119
    silicon in, 121
Manganese bronze, manganese in, 82
  in aluminium alloys, 100
  in copper alloys, 82
  in ferrous alloys, 19, 55
  in magnesium alloys, 19, 119
  in steel, 19, 55
      difference method, 19
      permanganic acid test for, 2
      silver persulphate reaction for, 19, 55
      specimen conversion table for, 23
Mercury vapour lamp, 8, 11, 25, 40, 46, 50, 55, 57, 61, 65, 73, 98, 100, 103, 106, 112, 116, 118, 121, 124
      advantages of, 11
      calibration with, 24, 25
      filters for use with, 11
      fitting and connections, 14
      principal radiators, 11
      warming up, 14
Metals, H. H. P., 22
Molybdenum blue test, 2, 65, 103, 121
      in ferrous alloys, 57
Monochromator, 36

N

Nickel in aluminium alloys, 100
    copper alloys, 85
    ferrous alloys, 62
  silvers, manganese in, 82

Operating the Spekker Absorptiometer, 12
Organic reagents, variability of, 27

P

Pipettes, 35
Phosphorus in copper alloys, 87
  in phosphor bronze, 27
  phospho-molybdate,
Photo cells, use of, 5, 36
Photo-electric colorimeters (see Absorptiometers), 5, 36
Photometric chemical analysis, 2
Pulfrich Photometer, 4, 6

Reaction, alizarin S, 110
  diethyldithiocarbamate, 50, 92, 112
  dimethylglyoxime, 50, 62, 85, 100
  diphenylcarbazide, 41
  nitroso-R-salt, 47
  permanganic acid, 82, 98, 119
  pertitanic acid, 68, 107
  pervanadic acid, 71
  phosphomolybdate complex, 88
  silico-molybdate molybdenum blue 65, 103, 121
  silver persulphate, 43, 55
  thiocyanate, 57, 80, 95, 116
Reagents for absorptiometry, 22
      need for purity, 27
  organic, variability of, 27

S

Silicon determinations, 30
  in aluminium alloys, 103
  in magnesium alloys, 121
  in steel alloys, 65
Spectrophotometers, 4
Spectrophotometry, 2
Spectrum filters, Ilford, 9
      transmission data, 10
Spekker Absorptiometer, 4, 6, 12 *et seq.*
Spekker Acid, 40, 47, 55, 57, 62, 71
Spot Galvanometer, 6, 36
Standard Alloys, 35
  Solutions, 21, 22
Stainless steel (18-8) analysis, 56
Stannous chloride stains cells, 60
Steel (see also Ferrous Alloys)
  carbon in, 2
  high speed, 40
  "66" substitute high speed, analysis, 59
  silicon in, 65

T

Temperature, and time effect on calibration solutions, 26
Titanium in aluminium alloys, 107
  in ferrous alloys, 68
Tungsten filament lamp, 8, 39 (and in separate analyses)
      fitting and connections, 14

Vanadium in ferrous alloys, 71
Variable calibrated aperture, 6

W

Water cell, 7, 16
Water-to-Water setting of Absorptiometer, 17
      variations of, 30, 32
Wavelengths of Mercury radiations, 11
Wood's glass filter, 11
Working cabinet for Absorptiometer, 12
Wratten filters, 11

Zeiss Pulfrich Photometer, 4